An Investigation of some Group Three Halides
with various Donor Molecules
including a Thermodynamic Study of Carbonyl Bromide
and some Aluminium Halides

A thesis submitted by

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in canditature for the degree of Doctor of Philosophy
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DEDICATION

To my parents, and to everybody who has helped
me along the way.

ABSTRACT

The interaction between boron trihalides (bromide, chloride) and benzene derivatives (benzene, m-xylene, mesitylene, hexamethylbenzene) has been studied using the techniques of cryoscopy, vapour pressure measurement, proton magnetic resonance and Raman spectroscopy. No evidence was found to support previous assertions of weak complex formation in solution.

The reactions between carbonyl halides (bromide, chloride) and Group Three halides (boron, aluminium; chloride, bromide, iodide) have been studied. No complexes could be isolated, in contrast to the system $COCl_2/AlCl_3$ studied previously. No reaction was found using boron halides, but with aluminium halides rapid and extensive halogen exchange occurred at ambient temperatures. Aluminium halides also catalysed the decomposition of carbonyl bromide:

$$COBr_2(L) = CO(g) + Br_2(g) [+ Br_2(L)]$$

The enthalpy of hydrolysis of carbonyl bromide was measured by adiabatic solution calorimetry

$$COBr_2(l) + nH_2O \longrightarrow CO_2(g) + [2HBr.(n-1)H_2O](l)$$
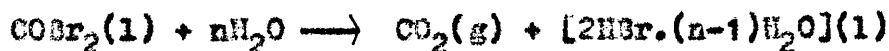
ΔH^o hydrolysis $= -49.06 \pm 0.16$ kcal mol^{-1}

$$[-205.36 \pm 0.67 \text{ kJ mol}^{-1}]$$

From this was derived

$$\Delta H_f^O \ COBr_2(l) = -34.70 \pm 0.21 \text{ kcal mol}^{-1} \ [-145.18 \pm 0.88 \text{ kJ mol}^{-1}]$$
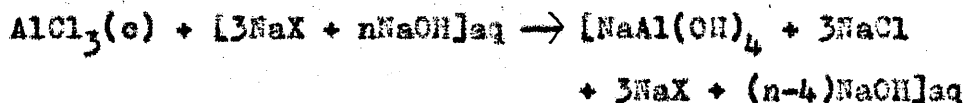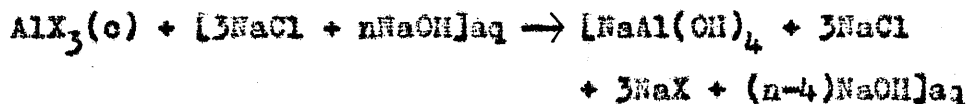
differing significantly from previous values. Estimates have been made of thermodynamic functions for carbonyl iodide.

The standard enthalpies of formation of aluminium bromide and aluminium iodide have been determined as

$$\Delta H_f^O \ AlBr_3(c) = -118.4 \pm 0.6 \text{ kcal mol}^{-1} \ [-495.2 \pm 2.4 \text{ kJ mol}^{-1}]$$

$$\Delta H_f^O \ AlI_3(c) = -67.1 \pm 0.6 \text{ kcal mol}^{-1} \ [-280.9 \pm 2.4 \text{ kJ mol}^{-1}]$$

by isoperibol calorimetry of the reactions

$$AlX_3(c) + [3NaCl + nNaOH]aq \longrightarrow [NaAl(OH)_4 + 3NaCl + 3NaX + (n-4)NaOH]aq$$

$$AlCl_3(c) + [3NaX + nNaOH]aq \longrightarrow [NaAl(OH)_4 + 3NaCl + 3NaX + (n-4)NaOH]aq$$

where X = Br or I. In addition,

$$\Delta H_f^O \ NaAl(OH)_4 \cdot 15,000 \ H_2O = -409.9 \pm 0.4 \text{ kcal mol}^{-1} \ [-1715.0 \pm 1.6 \text{ kcal mol}^{-1}]$$

Infra-red studies on the complex $POCl_3 \cdot BCl_3(c)$ have confirmed its structure as dative covalent, with bonding from oxygen to boron. On running the infra-red spectrum at room temperature, there is considerable dissociation of the complex, and also reaction with the potassium bromide windows. Determination of the degree of dissociation has shown that there is only negligible association in the vapour.

CONTENTS

DIAGRAMS

DIAGRAMS (continued)

PART ONE

THE INTERACTION BETWEEN BORON TRIHALIDES

AND BENZENE DERIVATIVES

INTRODUCTION

Previous work[1,2] has suggested the presence of weak solute-solvent complexing in benzene solutions of boron tribromide and boron tri-iodide. In each case, the symmetric stretching mode, ν_1, (278 cm^{-1} BBr$_3$, 196 cm^{-1} BI$_3$) of the boron trihalide appeared as a strong band in the infra-red spectrum. Since the selection rules predict Raman activity only for this mode, it was suggested that deformation of the boron trihalide was allowing the band to become active.

[11]B nuclear magnetic resonance of the boron tribromide/ benzene system showed a residual high-field shift at infinite dilution of 0.48 p.p.m. (relative to pure boron tribromide) after correcting for the bulk diamagnetic susceptibility of the system, again suggesting weak interaction. It was proposed that the principal orientation of boron was above or below the plane of the aromatic ring, as indicated in the following diagram:-
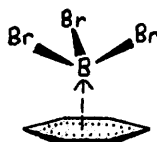
The average distance between the aromatic ring and the boron atom was estimated to be 4.7$\overset{o}{A}$.

However, the same workers state that the phase diagrams for boron tribromide + benzene and boron tri-iodide + benzene showed no sign of complex formation.

The object of the present work was to seek further evidence for complex formation, using the following techniques:-

(1) Cryoscopy, and determination of phase diagrams.

(2) Vapour Pressure Measurement.

(3) Proton Magnetic Resonance.

(4) Raman Spectroscopy.

Boron trichloride and boron tri-iodide were studied with the following aromatic compounds; benzene, m-xylene, mesitylene and hexamethylbenzene. The electron-donating methyl group should increase the Lewis basicity of the aromatic ring.

(1) PHASE DIAGRAMS

The apparatus was tested using the known chloroform/ mesitylene system[5], and then the mixtures

    boron tribromide/mesitylene,

    boron tribromide/m-xylene,

and boron tribromide/hexamethylbenzene

were studied.

Experimental

Apparatus:-

The cryometer used (diagram 1) has been described in detail elsewhere.[3] Temperature was measured using a miniature platinum resistance thermometer (Degussa Hanau) connected across one arm of a Wheatstone bridge, and calibrated using the freezing points of purified (see next paragraph) chlorobenzene (-45.2°C) and chloroform $(-63.5^{\circ}$C$)^{[4]}$ (diagram 2). Readings were accurate to $\pm$ 0.1°C. Stirring was achieved by means of a solenoid-activated, reciprocating, chromium-plated, iron cylinder.

Chemicals:-

Chlorobenzene (May and Baker) was dried over size $4\overset{o}{A}$ molecular sieves and distilled at atmospheric pressure (b.p. 131.5°C, literature[4] 131.7°C).

Chloroform (May and Baker) was shaken with water to remove added alcohol, dried over $4\overset{o}{A}$ molecular sieves, and distilled (b.p. 61.2°C, literature[4] 61.2°C).

Mesitylene (B.D.H. Ltd.) was dried over $4\overset{o}{A}$ molecular sieves and distilled (b.p. 164.7°C, literature[4] 164.7°C).

M-xylene (B.D.H. Ltd.) and hexamethylbenzene (Koch-Light) were used as supplied commercially, with stated purities of at least 99% and 98% respectively.

DIAGRAM 1

CRYOSCOPIC APPARATUS

rubber
cap

air
jacket

glass—
coated
iron

CELL

PLATINUM
RESISTANCE
THERMOMETER

STIRRER
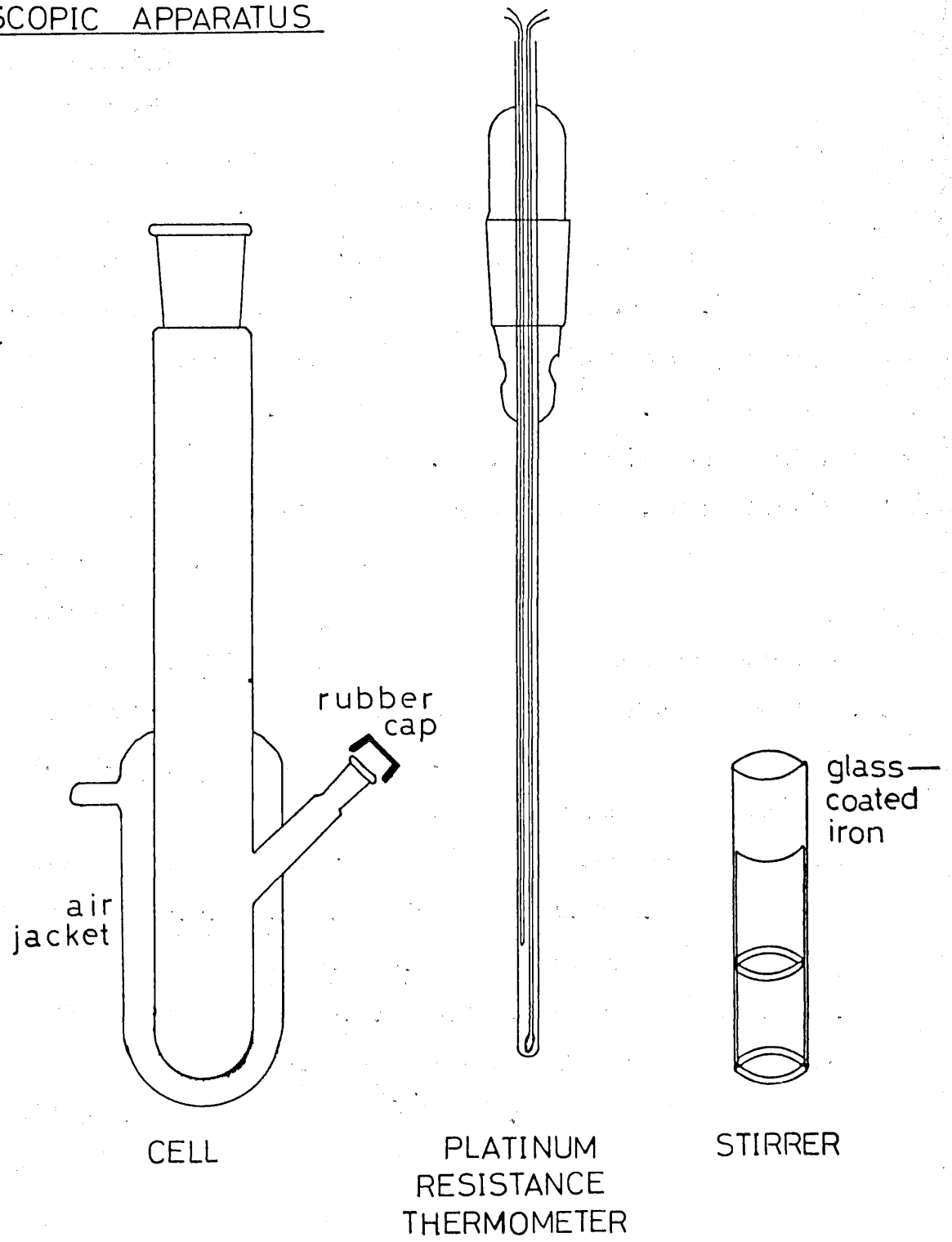
DIAGRAM 2

CALIBRATION OF

PLATINUM RESISTANCE THERMOMETER

15
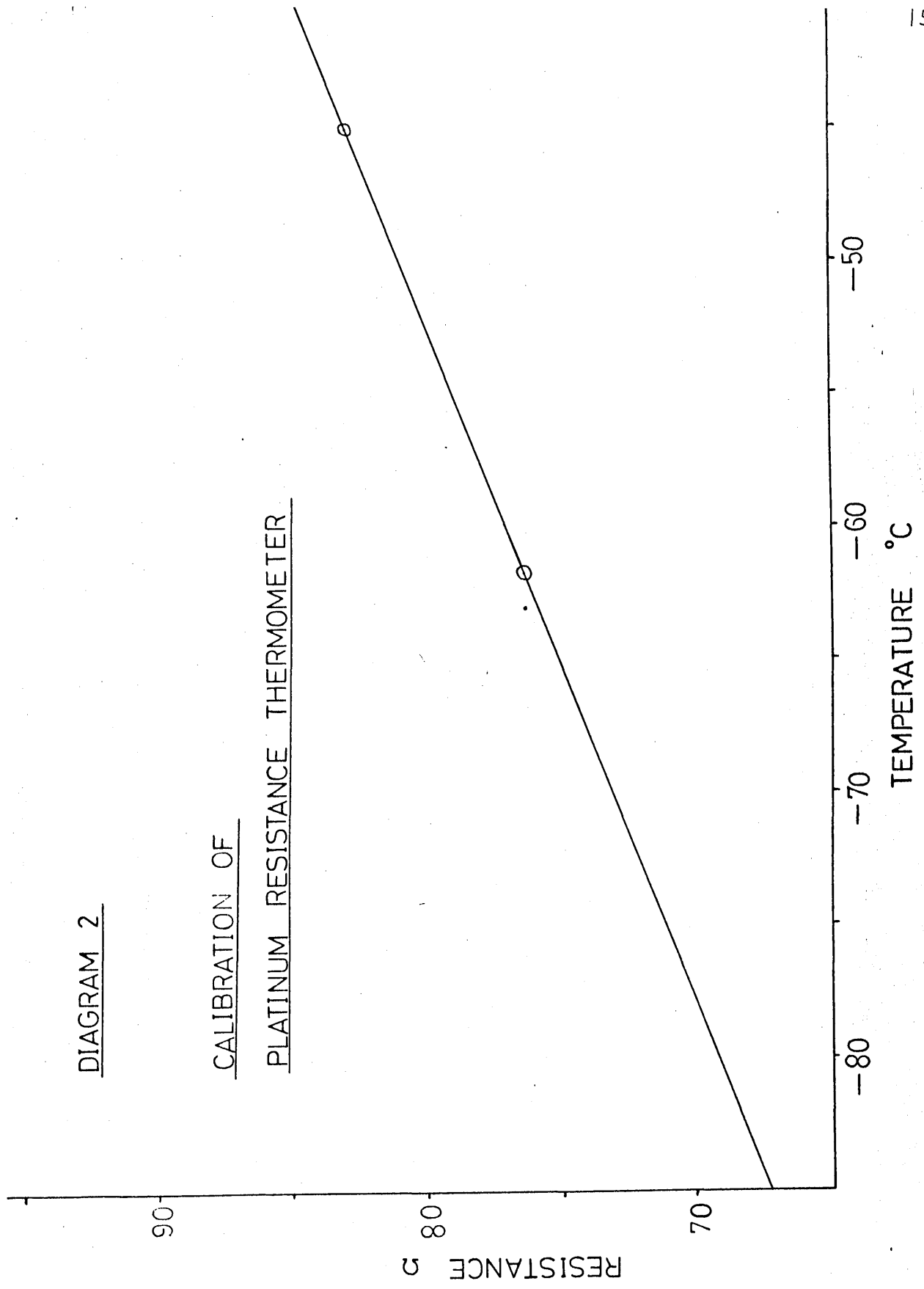
Boron tribromide (Koch-Light) was purified by shaking with mercury to remove any free bromine, and then distilled at atmospheric pressure, the portion boiling at 91 ± 1°C being retained, (literature b.p.[4] 91.3°C).

Procedure :-

One component was placed in the cryometer, and successive aliquots of the second component added through the side-arm. Moisture sensitive boron tribromide was always loaded in the cryometer in a dry-box, the side-arm covered with a self-sealing rubber cap, and the hydrocarbon aliquots added through the cap using a repeater syringe (Jencons Ltd.), weighed before and after each addition. The quantity of boron halide used was determined by post-experiment hydrolysis with water, separation of the hydrocarbon, and titration for bromide with 0.1N silver nitrate solution, using eosin indicator.

The mixture was frozen using a toluene/liquid nitrogen slush bath (ca -94°C). The freezing point was taken when the temperature remained almost constant for approximately one minute, or longer, due to the latent heat of fusion evolved. Where supercooling occurred, the temperature fell well below the freezing point, and then rose sharply as crystallisation commenced, falling again when equilibrium had been reached. The freezing point was taken as the maximum temperature reached after crystallisation[6].

Results and Discussion

Chloroform + Mesitylene

The results of a single experiment are given in Table 1.

TABLE 1

FREEZING POINTS OF CHLOROFORM + MESITYLENE MIXTURES

P.R.T. RESISTANCE (OHMS ± 0.1 OHM)	FREEZING POINT (^{o}c ± 0.1^{o}c)	MOLE FRACTION % CHLOROFORM
75.8	-63.5	100.0
73.1	-70.9	89.5
72.8	-71.5	87.3
72.2	-73.5	80.9
72.8	-71.5	77.4
75.4	-64.6	73.9
76.8	-60.8	69.6
79.1	-55.4	63.2
80.1	-52.8	57.9
80.9	-50.4	53.4
81.0	-50.3	49.5
80.8	-50.4	46.2
73.6	-56.5	34.7
75.1	-65.7	26.1
74.9	-66.1	15.5
79.2	-54.6	0.0

The freezing points for pure chloroform and pure
mesitylene agree very well with literature[4] values of

FREEZING POINT—COMPOSITION CURVE

FOR CHLOROFORM/MESITYLENE

DIAGRAM 3

FREEZING POINT °C

−50

−70

MOLE FRACTION % CHLOROFORM

20   40   60   80   100
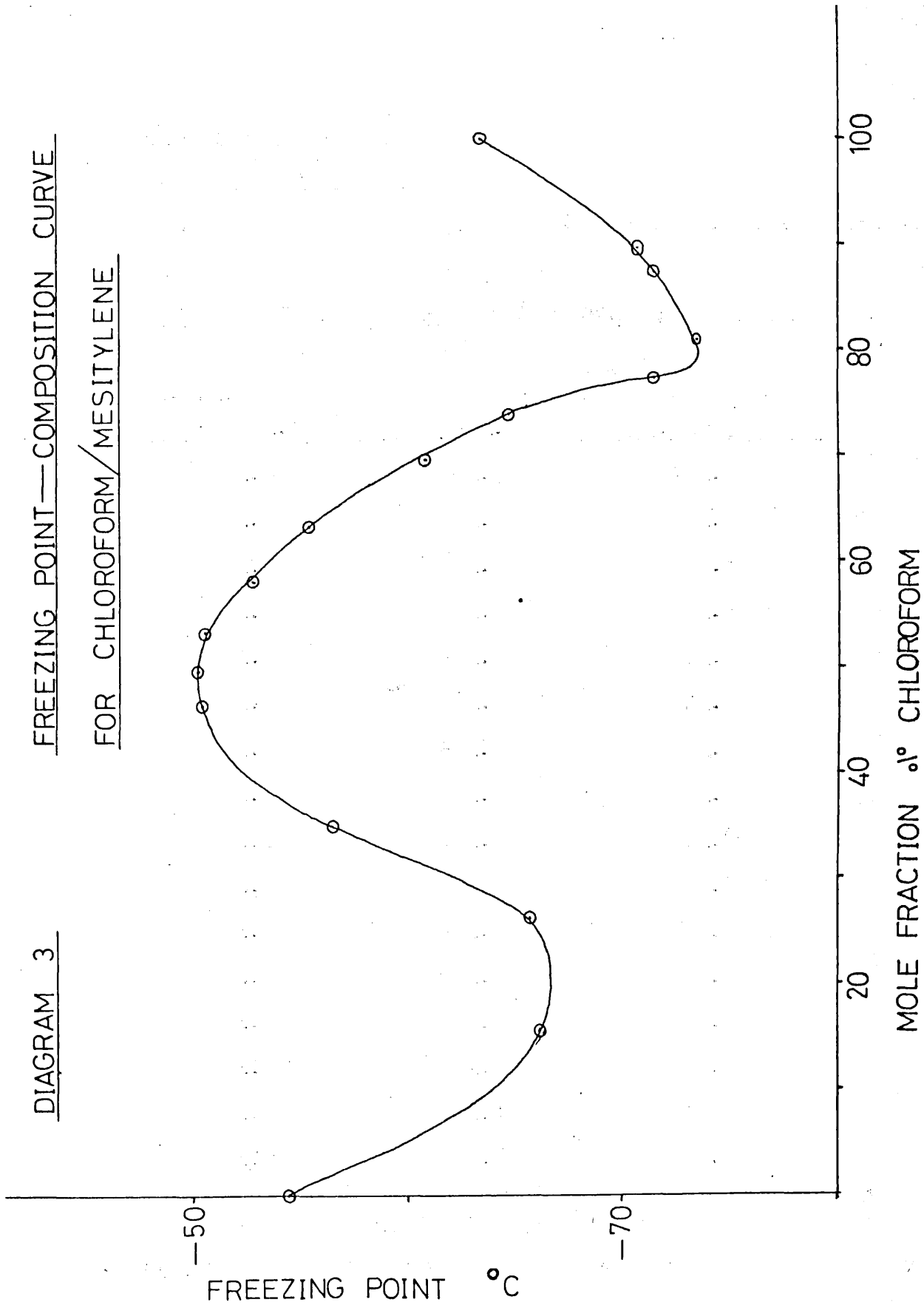
-63.5°C and -52.7°C respectively.

The phase diagram (diagram 3) shows a well-defined peak at 50 mole % chloroform, indicating a 1:1 complex with a congruent melting point[7]. In effect, this corresponds to two eutectic phase diagrams linked together, namely, for chloroform + complex and complex + mesitylene. The diagram agrees well with previous results[5].

Boron Tribromide + Mesitylene

On mixing boron tribromide and mesitylene, both of which were colourless, a very pale lemon-yellow colour appeared, which deepened considerably on freezing the mixture.

In all, six experiments were carried out, the results of which are given in Table 2.

The results show very poor reproducibility below approximately 50 mole % boron tribromide (diagram 4). The reason for this is not entirely clear. One possible explanation is that supercooling, which was particularly marked in this area, resulted in the true freezing point not always being reached, upon commencement of crystallisation[6]. Crystals of mesitylene, being in excess, would tend to separate, so that by the time equilibrium was reached the liquid present would be richer in boron tribromide, and the freezing point correspondingly lower. Hence the correct freezing point would never be attained.

TABLE 2

FREEZING POINTS OF BORON TRIBROMIDE/MESITYLENE MIXTURES

EXPERIMENT NUMBER	P.R.T. RESISTANCE (OHM ± 0.1 OHM)	FREEZING POINT (°c ± 0.1°c)	MOLE FRACTION % BORON TRIBROMIDE
1	82.7	-46.0	100.0
1	81.0	-50.2	90.8
1	79.3	-55.0	83.1
2	77.5	-59.3	74.5
6	77.0	-60.5	73.0
1	76.8	-61.0	71.1
1	74.7	-66.7	62.1
2	73.8	-68.8	59.3
6	73.7	-69.5	57.4
1	73.1	-70.9	55.2
6	71.9	-73.8	51.9
1	71.7	-74.4	49.6
5	69.6	-80.2	49.5
2	71.3	-75.5	49.3
3	70.5	-77.7	47.9
6	70.7	-77.1	47.4
3	70.4	-77.7	45.9
1	69.9	-79.2	45.1
3	70.5	-77.7	44.0
6	69.1	-81.0	43.5
2	68.9	-81.6	42.2
3	70.4	-77.7	42.2
6	69.0	-81.3	40.3
5	69.5	-80.2	39.6
2	68.9	-81.6	36.8
4	68.4	-82.2	36.8
5	69.4	-80.2	32.9
2	68.9	-81.6	32.7
3	70.5	-77.7	29.8

DIAGRAM 4

FREEZING POINT—COMPOSITION CURVE

FOR BORON TRIBROMIDE/MESITYLENE
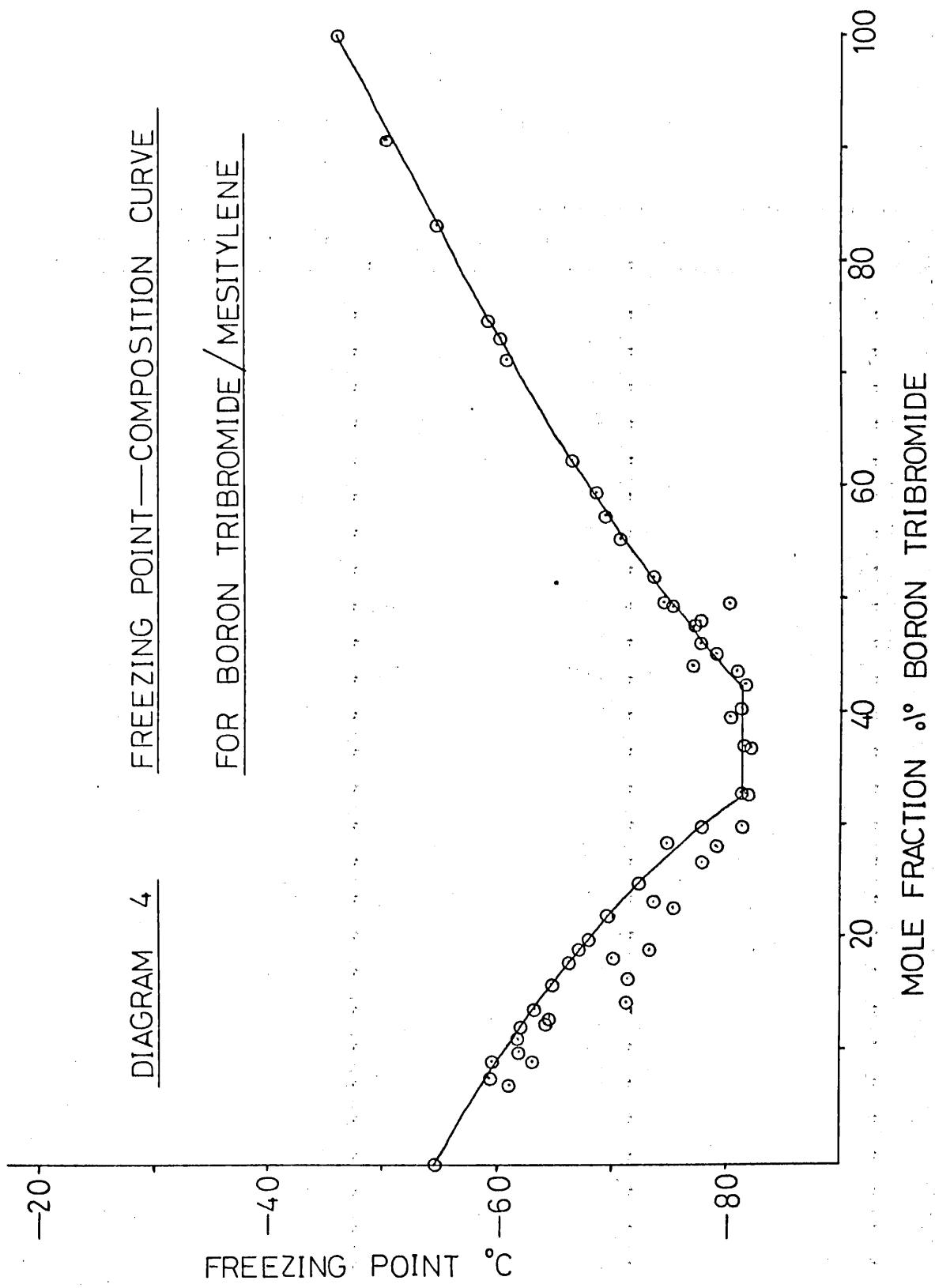
TABLE 2 (CONTINUED)

EXPERIMENT NUMBER	P.R.T. RESISTANCE (OHM ± 0.1 OHM)	FREEZING POINT (°C ± 0.1°C)	MOLE FRACTION % BORON TRIBROMIDE
1	69.3	-80.5	29.4
5	71.6	-75.0	28.2
4	69.9	-79.1	28.0
2	70.7	-77.1	26.7
5	72.5	-72.5	24.7
2	72.4	-72.6	24.5
3	72.0	-73.7	23.0
4	71.4	-75.3	22.6
5	73.5	-69.8	21.9
5	74.0	-68.4	19.7
4	72.2	-73.3	18.9
3	74.3	-67.5	18.7
2	73.4	-70.0	18.3
5	74.7	-66.6	17.9
4	72.9	-71.3	16.3
3	75.4	-64.6	15.8
4	72.9	-71.3	14.3
3	75.9	-63.4	13.7
4	75.5	-64.5	12.7
5	75.6	-64.2	12.3
3	76.5	-62.0	12.0
3	76.6	-62.0	10.7
3	76.6	-62.0	9.7
4	76.0	-63.0	8.9
3	77.3	-59.6	8.9
3	77.3	-59.6	7.5
4	76.8	-61.1	6.8
-	79.2	-54.6	0.0

The true freezing point is thus taken as the highest value obtained for any given composition, when a reasonably smooth curve is obtained.

A plateau is clearly discernible between approximately 33-43 mole % boron tribromide, but there is no evidence for a peak due to complex formation. The plateau is probably due to a miscibility gap[7,8], containing, at equilibrium, two solids in equilibrium with the remaining liquid. [On complete solidification, a heterogeneous mixture of the two solids would presumably be obtained]. By applying the Phase Rule to this equilibrium[7,8], we obtain, for three phases and only two components, one degree of freedom. This is taken up by the pressure of the system, assumed constant. This means that whatever the composition of the mixture within this range, the temperature of freezing must remain constant. A similar incongruency was found in the boron tri-iodide/benzene phase diagram[2].

Boron Tribromide + m-Xylene

Again, a yellow colour was observed, but only in the solid phase.

The results of a single run are given in Table 3.

The literature[4] freezing point for m-xylene is $-47.4^{o}C$. The freezing point-composition curve (diagram 5) shows a simple eutectic at $-79^{o}C$, where the composition is 47% boron tribromide, 53% m-xylene. There is no miscibility gap as for

FREEZING POINT—COMPOSITION CURVE

FOR BORON TRIBROMIDE/m-XYLENE

DIAGRAM 5

FREEZING POINT °C

MOLE FRACTION % BORON TRIBROMIDE

24
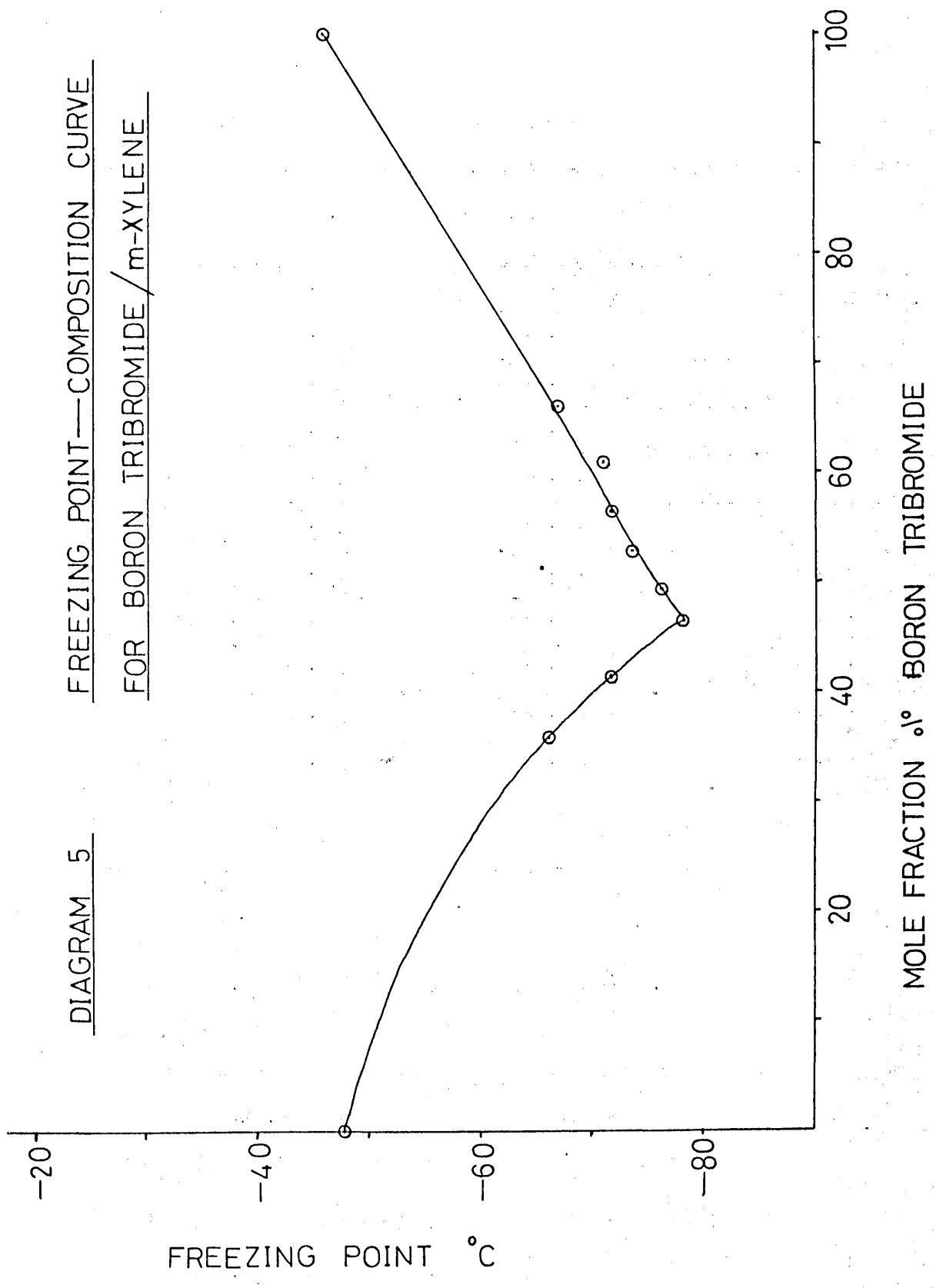
TABLE 3

FREEZING POINTS OF BORON TRIBROMIDE/m-XYLENE MIXTURES

P.R.T. RESISTANCE (OHMS ± 0.1 OHM)	FREEZING POINT (°C ± 0.1°C)	MOLE FRACTION % BORON TRIBROMIDE
82.7	-46.0	100.0
74.6	-67.0	66.0
73.0	-71.1	60.8
72.8	-71.8	56.4
72.1	-73.5	52.6
71.0	-76.4	49.3
70.3	-78.2	46.3
72.7	-71.8	41.4
74.8	-66.2	35.7
82.0	-47.5	0.0

boron tribromide/mesitylene, and no evidence for complex formation.

Boron Tribromide + Hexamethylbenzene

A similar phase diagram could not be obtained, due to the very low solubility of solid hexamethylbenzene in boron tribromide i.e. the presence of a wide miscibility gap. All solutions prepared at room temperature and cooled, gradually precipitated hexamethylbenzene to give saturated solutions of approximate composition 1 mole % hexamethylbenzene, 99 mole %

tribromide, and freezing at -47.6°C.

On mixing hexamethylbenzene (a white solid) with boron tribromide (a colourless liquid), an orange colour appeared in the solutions obtained.

(2) VAPOUR PRESSURE MEASUREMENTS

The systems studied were:-

Boron tribromide + benzene

Boron tri-iodide + benzene

Boron tribromide + mesitylene.

Experimental

Apparatus:-

All the compounds were handled on a vacuum line capable
of achieving pressures of 10^{-4} torr or better (diagram 6).
Mixing of the compounds, and all vapour pressure measurements,
took place in a section of the line completely free from
grease, thereby avoiding any absorption of the grease or
reaction with boron tribromide. Under these conditions, best
vacuum seals were obtained by using taps of the "Uni-form"
type (Glass Precision Engineering Co. Ltd.,), and "O-ring"
joints (J. Young (Scientific Glassware) Ltd.). Thus the
compounds were exposed only to Teflon, glass and mercury vapour
(from the manometer). Vapour pressures were determined using
a mercury manometer, consisting of two parallel glass tubes,
approximate diameter 2 cm, connected by a capillary tube.
The mercury was carefully degassed before use by pumping for
several hours while warming gently. The difference in height
of the two mercury columns was measured using a cathetometer.
Pressures were usually reproducible to $\pm$ 1 torr.

DIAGRAM 6   VACUUM SYSTEM FOR

VAPOUR PRESSURE MEASUREMENTS

To
Pump

Benzene

Mixing
Vessel

Mercury
Manometer

Boron
Tribromide

Greaseless
Tap

28
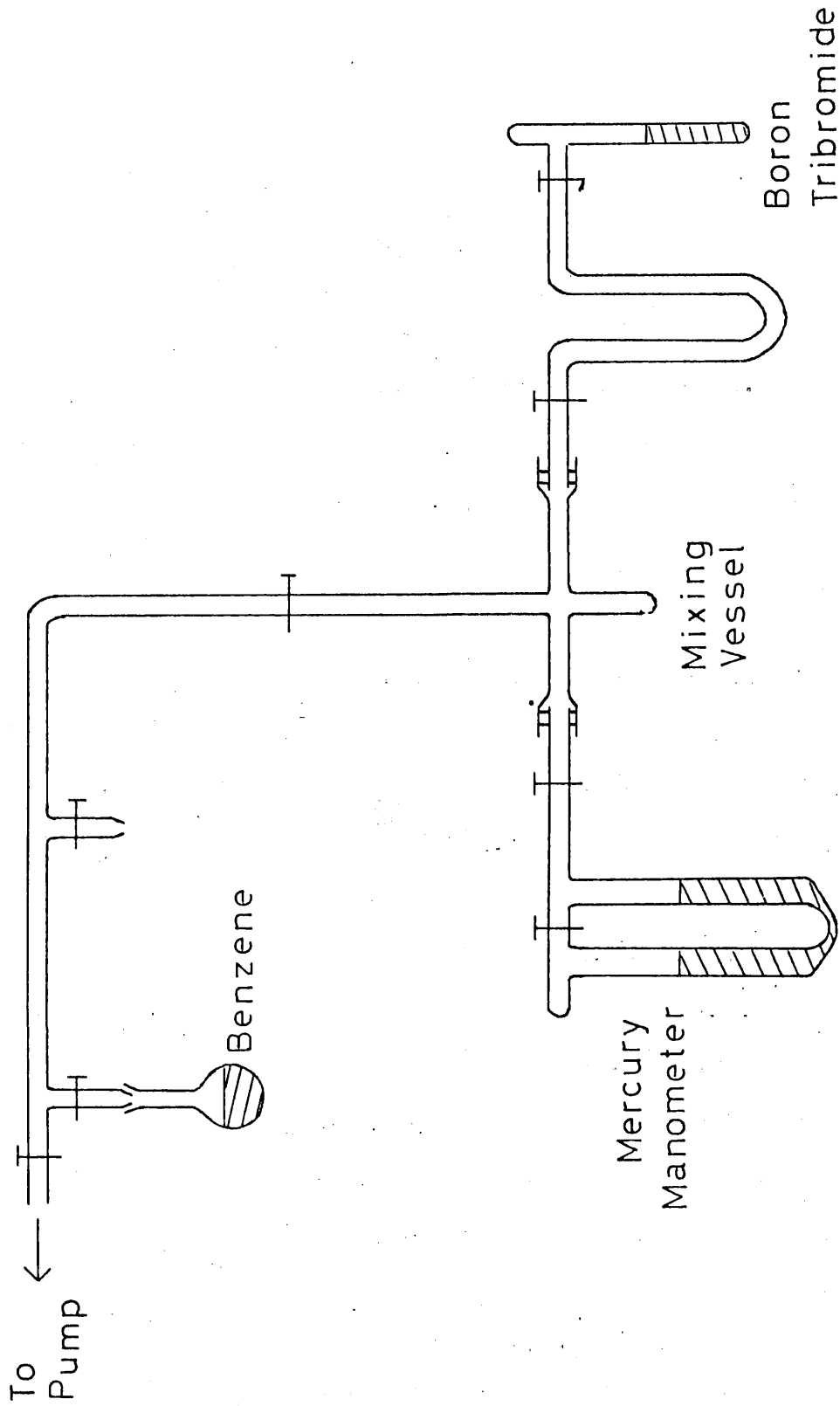
Chemicals:-

Distilled boron tribromide, b.p. 91°C (literature[4] 91.5°C)
was redistilled into its container on the vacuum line, where it
was stored over mercury to remove any free bromine formed.
It was degassed by repeated freezing and pumping. Before each
run, the sample used was distilled and trapped at ca. -80°C
(solid carbon dioxide - acetone slush bath), at which tempera-
ture any hydrogen bromide impurity would be pumped off
(vapour pressure[4] $\sim$ 500 torr). It was then condensed into
the mixing vessel, and its purity checked by measurement of
its vapour pressure at known temperatures:-

Temp. (°C)	Experimental V.p. (torr)	Lit. Value[9] (torr)
0	19	19
12.8	37	35
20	52	54

A supply of pure boron tri-iodide was already available
in the laboratory, with established purity[1,2] 98-99%.

Commercial samples of benzene and mesitylene (B.D.H. Ltd.)
were distilled (b.p. 80.0°C and 164.7°C respectively, liter-
ature values[4] 80.1°C and 164.7°C), and dried and stored over
grade 4Å molecular sieves (B.D.H. Ltd.). Each was degassed
by repeated freezing and pumping. The purity was also
checked by measurement of vapour pressure:-

Temp. (^{o}C)	Experimental V.p. (torr)	Lit. value[4,10](torr)
Benzene 0.0	25	26.3
12.8	52	52.5
20.5	79	76.7
Mesity- 19 lene	2	1.7

Procedure :-

A quantity of boron trihalide was either condensed into the mixing vessel, (BBr_3) or loaded in a dry-box and then connected to the vacuum line and degassed (BI_3). Aliquots of benzene or mesitylene were then distilled in, the amount added being determined by weighing the container before and after each addition. The mixture was now isolated from the pump, and allowed to come to equilibrium at the temperature selected for the pressure measurements. Readings were usually taken below room temperature to avoid thermostating the manometer. To achieve this, either an ice bath (0 ± 1°C) or a p-xylene/liquid nitrogen slush bath (13 ± 1°C) was used. In the case of boron tribromide + mesitylene, consistent readings were only obtained when the mixture was well stirred. The reason for this is not known. To achieve mixing, a magnetic stirrer and glass-coated follower were used, which meant however that the mixture could not be thermostated, and all readings had to be taken at room temperature.

The quantity of boron halide used was determined by post-experiment hydrolysis and titrimetric analysis. At the end of each run, the mixture was frozen in liquid nitrogen, and the mixing vessel cut off using a hot spot. The mixture was then analysed argentimetrically, as described previously (page 16), for halide.

Results and Discussion

Boron Tribromide + Benzene

A colourless solution resulted from mixing boron tribromide and benzene, which remained colourless on freezing, in contrast to the other systems studied.

Four experiments were performed, and the results shown in Table 4.

The results from experiment 1 were in very poor agreement with the rest, and were discarded in constructing the pressure - composition curves (diagram 7). These show a positive deviation from Raoult's Law:-

$$P = N_A p_A + N_B p_B$$

N_A = Mole fraction component A

p_A = Partial pressure component A

P = Observed pressure.

DIAGRAM 7   VAPOUR PRESSURE OF
BORON TRIBROMIDE / BENZENE
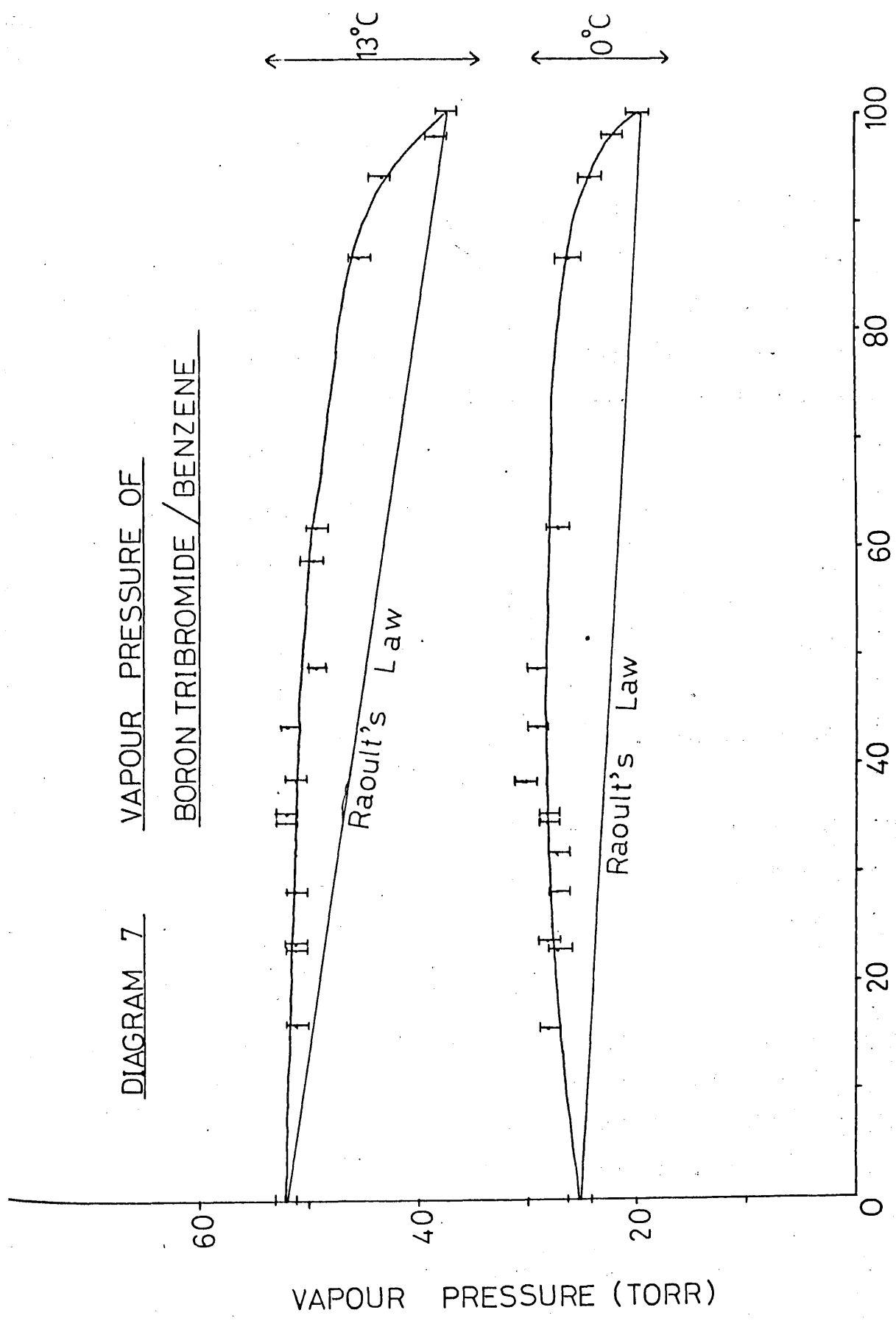
TABLE 4

VAPOUR PRESSURES OF BORON TRIBROMIDE/BENZENE MIXTURES

EXPERIMENT NUMBER	VAPOUR PRESSURE (TORR ± 1 TORR)		MOLE FRACTION % BORON TRIBROMIDE
	$0°C \pm 1°C$	$13°C \pm 1°C$	
1	19	–	100.0
2	19	37	100.0
3	22	38	97.9
3	24	43	94.0
3	26	45	86.5
3	27	49	61.6
1	41	–	58.6
2	29	49	48.8
3	29	52	43.4
2	30	51	38.3
3	28	52	35.4
2	28	52	34.6
2	27	51	31.7
4	27	51	28.2
4	28	51	23.7
2	27	51	22.9
1	31	–	21.6
4	28	51	15.7
1	32	–	11.4
1	30	–	8.3
5	25	52	0.0

This implies that the major contribution to interaction between boron tribromide and benzene in the liquid phase comes from   Van der Waal's forces.   An alternative representation[7] is that the attraction between two molecules of the same component is greater than between two different molecules. If any significant complex formation occurred, a negative deviation would be expected.

Boron Tri-iodide + Benzene

Great difficulty was experienced in dissolving boron tri-iodide, even with vigorous stirring.   Consequently, measurements were only possible at 13°C, and then only at concentrations below 30 mole % boron tri-iodide.

The solutions were colourless, and remained so on freezing.

The results of the single experiment are given in Table 5.

TABLE 5

VAPOUR PRESSURE OF BORON TRI-IODIDE + BENZENE

VAPOUR PRESSURE (TORR ± 1 TORR) 13°C ± 1°C	MOLE FRACTION % BORON TRI-IODIDE
2	100.0
43	28.6
48	13.4
49	9.6
52	0.0

VAPOUR PRESSURE OF

BORON TRI-IODIDE / BENZENE

DIAGRAM 8

VAPOUR PRESSURE (TORR)

60

40

20

MOLE FRACTION % BORON TRI-IODIDE

0   20   40   60   80   100
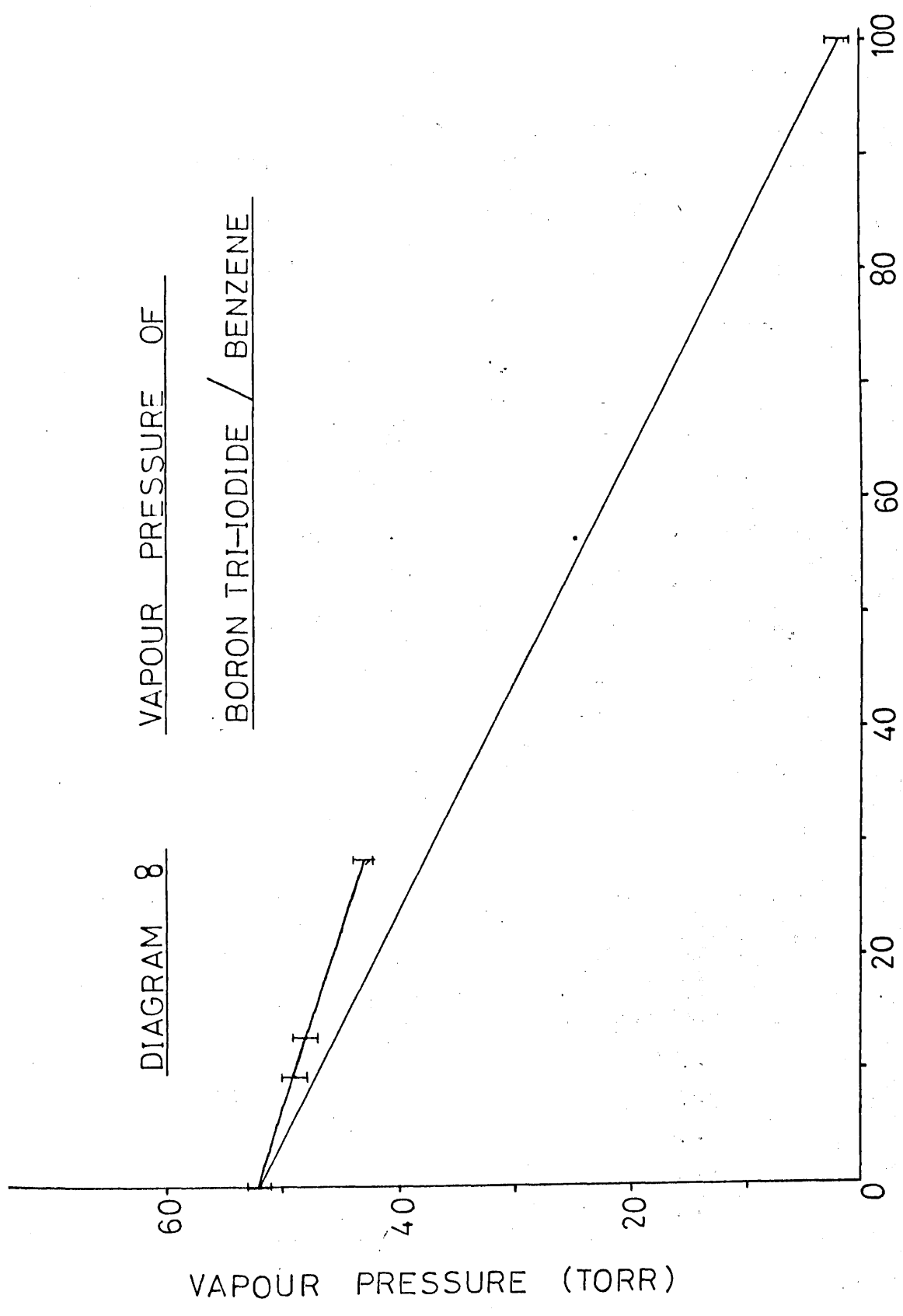
Despite the small number of points, and the fact that only one-third of the total composition range is covered, the pressure-composition curve (diagram 8) shows a clear positive deviation from Raoult's Law. Again, there is no support for complex formation.

Boron Tribromide + Mesitylene

As in the cryoscopic experiments, a yellow colour, particularly pronounced in the solid phase, appeared on mixing the two components.

Because of the necessity for stirring to obtain consistent pressure measurements, readings were only taken at room temperature, $19^{\circ}C$. The results are shown in Table 6.

TABLE 6
VAPOUR PRESSURE OF BORON TRIBROMIDE + MESITYLENE MIXTURES

VAPOUR PRESSURE (TORR $\pm$ 1 TORR) $19 \pm 1^{\circ}C$	MOLE FRACTION % BORON TRIBROMIDE
52	100.0
37	64.3
36	61.7
33	49.7
26	35.0
25	32.5
2	0.0

As with the previous experiments, there is a positive deviation from Raoult's Law, and no evidence of complexing (diagram 9).

DIAGRAM 9

VAPOUR PRESSURE OF

BORON TRIBROMIDE / MESITYLENE
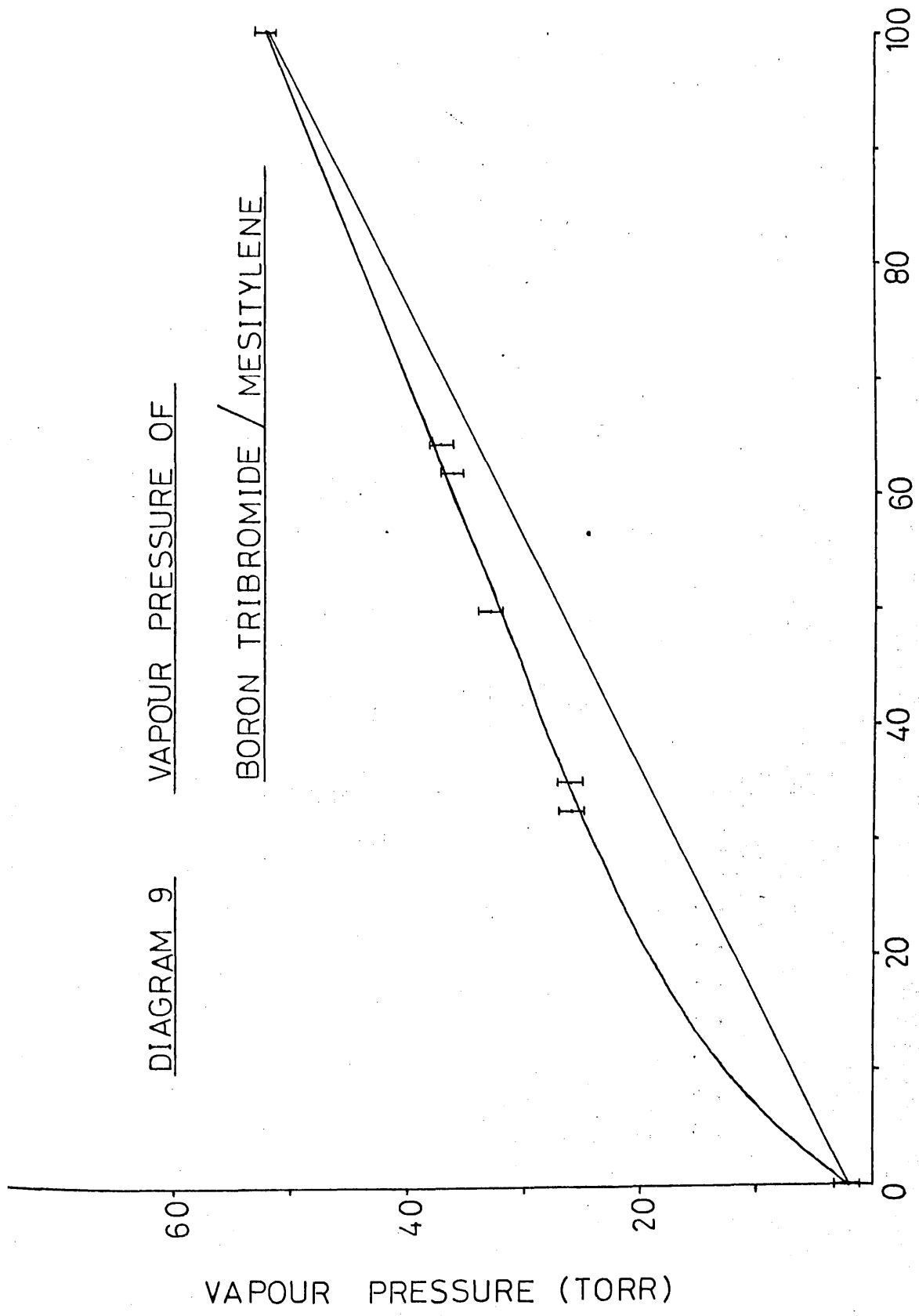
VAPOUR PRESSURE (TORR)

MOLE FRACTION % BORON TRIBROMIDE

(3) PROTON MAGNETIC RESONANCE

[1]H shifts were determined for mesitylene, and a 1:1 mixture of mesitylene and boron tribromide, using tetramethylsilane (T.M.S.) as internal standard. For comparison, the 1:1 mesitylene/chloroform spectrum was also run.

Experimental

Chemicals:-

Mesitylene, chloroform and boron tribromide were purified as described previously (p. 29). Tetramethylsilane was used as obtained commercially (B.D.H. Ltd.).

Procedure:-

All the spectra were run on a Varian HA 60-IL machine (60 KHz), locked on to the T.M.S. peak, with facilities for low temperature spectra using a liquid nitrogen/nitrogen gas flow for cooling.

The N.M.R. tubes were filled with sample in a dry-box (including small quantities of T.M.S. as an internal standard), and then sealed.

Spectra were obtained for all three samples at room temperature, and also at -40°C for mesitylene and mesitylene/boron tribromide.

Results and Discussion

TABLE 7

PROTON MAGNETIC RESONANCE RESULTS

SYSTEM	INTENSITY RATIO	PROTON	CHEMICAL SHIFT				SPLITTING PATTERN
			Room temperature		$-40^{\circ}C$		
			H_z	p.p.m.	H_z	p.p.m.	
$C_6H_3(CH_3)_3$	3	CH_3	128.7	2.145	127.6	2.127	At least quartet.
	1	H	396.4	6.607	394.4	6.573	At least octet.
$C_6H_3(CH_3)_3$ + BBr_3	3	CH_3	129.2	2.153	128.4	2.140	At least quartet.
	1	H	396.8	6.613	395.0	6.583	At least octet.
$C_6H_3(CH_3)_3$ + $CHCl_3$	3	CH_3	130.0	2.167	-	-	At least quartet.
	1	H	400.6	6.677	-	-	At least octet.

All shifts are relative to TMS, and accurate to $\pm$ 0.3H_z (0.006 p.p.m.).

The separation between peaks due to splitting was $\sim$ 0.6H_z for each system.

The predicted spectrum for mesitylene[11] is two peaks with very complex splitting, since all the couplings are long range, small, and of the same order. However, the chemical shifts and observed splitting in the present case are in good agreement with published spectra for pure mesitylene.[11,12,13]

Before the shifts in the mixtures can be compared with those of pure mesitylene, allowance must be made for the variation in bulk magnetic susceptibility. This can be represented[14] as "preferred orientations" of the molecules in the mixtures arising not from any chemical interaction but from the inherent magnetic anisotropy of the molecules not averaging out to zero when all possible molecule-molecule orientations are considered. The correction is made using the equation[5,15,16]

$$\delta_{corrected} = \delta_{observed} + \frac{2}{3}\pi(\chi_{mixture} - \chi_{mesitylene})$$

where δ = shift in p.p.m.

χ = volume susceptibility

and[5]

$$\chi_{mixture} = N_A \chi_A + N_B \chi_B$$

The values used were

$$\chi_{mesitylene} = -0.652 \text{ c.g.s. units}[5]$$
$$\chi_{BBr_3} = -0.900 \text{ " } [1]$$
$$\chi_{CHCl_3} = -0.731 \text{ " } [5]$$

The effect of the TMS in this respect can be neglected, since it is only slightly affected by changes in bulk magnetic susceptibility, and it is present in only very low concentrations.

After making the corrections, the shifts obtained (relative to pure mesitylene as zero) are:-

TABLE 8

CORRECTED P.M.R. SHIFTS (MESITYLENE = 0)

SYSTEM	PROTON	CHEMICAL SHIFT (P.P.M.)	
		ROOM TEMPERATURE	$-40^{o}C$
MESITYLENE + BBr_3	CH_3	-0.24	-0.24
	H	-0.25	-0.24
MESITYLENE + $CHCl_3$	CH_3	-0.06	-
	H	-0.01	-

Due to the corrections made, shifts are now accurate to only ± 0.01 p.p.m.

All shifts are now up-field, showing more shielding, as expected. Aromatic protons or substituents are normally strongly deshielded by the field produced by the ring current[14,16], which opposes the applied field within the aromatic ring, but reinforces it outside the ring. Hence an up-field shift

suggests a weaker ring current, which would occur if there was interaction between the π-electron system and the Lewis acid.

However, the shifts are always only very slight, indicating that any interaction must be extremely weak. Compare, for example, with the complexes of 1,3,5 trinitrobenzene with benzene and methylbenzenes[17], where shifts of 1.2 - 1.3 p.p.m. are obtained for the ring protons. But negligible shifts are also obtained for solutions of iodine in benzene[18], where a weak charge-transfer interaction is also thought to occur[19].

Previous studies[1,5] on the shifts of the chloroform proton and [11]B of boron tribromide, both in mesitylene solution, gave values for 1:1 mixtures of -1.1 p.p.m. and -0.60 p.p.m. respectively, relative to pure chloroform and pure boron tribromide. The small values again suggest only weak interaction, though stronger than indicated by the present work. This is probably due to the change in shielding of the Lewis acid atom, sited directly above the π-electron cloud, being more pronounced than the indirect shielding of the ring substituents.

The identical shifts obtained at room temperature and -40°C for mesitylene/boron tribromide suggest little or no temperature dependence for any interaction. This is rather surprising, since the shift obtained would be a weighted average of the shifts for "complexed" and "free" molecules (assuming rapid exchange). [See, for example, reference 14, p.100]. One would expect an increasing proportion of molecules to be complexed as the temperature was lowered, with a corresponding increase in shift.

(4) RAMAN SPECTROSCOPY

The Raman spectrum of an approximately 1:1 mixture of boron tribromide and benzene was run in the region 0-300 cm^{-1}, while the sample was kept frozen, in order to detect the possible presence of lattice bands attributable to relative motion of molecules in the solid (see, for example, reference 20). Because of the large masses of the molecules involved, such lattice modes would be expected at very low frequencies.

Experimental

Spectra were run using a Carey 81 instrument, with a 50 mW Helium-Neon laser, and 6328Å exciting line.

The sample was placed in a flat-ended capillary, subsequently sealed. This was surrounded by a wal of plasticine to act as an insulating jacket, frozen by immersion in liquid nitrogen, and placed in the laser beam. Periodic visual checks were made to ensure that the sample remained solid.

Results and Discussion

Only two bands were obtained, at 153 cm^{-1} and 280 cm^{-1}, both strong in intensity. These are attributable to the ν_4 (in-plane bend) and ν_1 (symmetric stretch) modes of boron tribromide, which occur at 150 cm^{-1} and 273 cm^{-1} in liquid boron tribromide[21,22]. Benzene has no absorption in this region[23].

The absence of any further bands indicates that lattice bands must be so weak as to be indistinguishable from background noise.

CONCLUSIONS

While the results obtained eliminate the existence of strongly-bonded complexes between boron trihalides and benzene derivatives, the possibility of weak contact charge-transfer bonding[24,25] remains open.

The positive vapour pressure deviations from Raoult's Law, and the failure to find any discontinuities due to complexing in the phase diagrams suggest that the bonding energy must be extremely small, even by charge-transfer standards (for example, benzene/iodine is quoted[26] as -1.32 kcal/mol [-5.52 kJ/mole] and benzene/trinitrobenzene as -1.71 kcal/mol. [-7.15 kJ/mol]). A parallel can be drawn with the benzene/iodine system (see, for example, the reviews in references 19 and 27), where the bulk properties of the solutions show no deviations, but charge-transfer complexing is well established by other methods, such as infra-red and ultra-violet spectroscopy, spectrophotometry, X-ray crystallography, etc. Also, as already mentioned, there is no measurable shift in the benzene ^{1}H resonance on dissolving iodine[18].

Further support for loose complexing comes from the yellow colours observed when freezing many mixtures of boron tribromide and methylbenzenes. Absorption in the visible spectrum is a well-known phenomenon associated with charge-transfer complexes[19,24,28], caused by transitions between energy levels

associated with the charge-transfer bond. Indeed, the closely related systems aluminium bromide/benzene or methyl-benzenes have been shown to form 1:1 and 2:1 solid complexes, all of which are various shades of yellow[29,30].

Two approaches which might provide more evidence of complexing are the use of dipole moments and of ultra-violet spectral measurements of solutions of boron trihalides in benzenes. Both require further investigation. Many charge-transfer complexes, even when formed by molecular species each with very small individual dipoles, have been shown to exhibit appreciable dipole moments[31] (e.g. iodine/benzene). A determination[32] of the dipole moment of boron tribromide in benzene yielded a value of 0.194 e.s.u. Since very low values are unreliable it was inferred that the boron tribromide was planar However, in view of some of the other evidence, this needs re-investigating, along with other systems, in case the low value represents a real deviation from zero.

PART TWO

INTERACTION OF GROUP THREE HALIDES

WITH CARBONYL HALIDES

INTRODUCTION

Although reactions of boron and aluminium halides with organic carbonyls (and other organic ligands) have been extensively studied because of their importance in Friedel-Crafts type syntheses[33], with one exception very little work has been done on their reaction with carbonyl halides.

The exception is the system aluminium chloride/carbonyl chloride (phosgene). The first reference to this is in a paper by Band[34], who claimed the existence of several solid complexes varying from $Al_2Cl_6.5COCl_2$ to $2Al_2Cl_6.COCl_2$. In the light of later work, this paper seems very unreliable. Germann[35] and co-workers carried out extensive studies on the solutions, which contributed considerably to the formulation of acid-base theories for solvent systems[36,37,38]. Aluminium chloride/phosgene solutions were believed to contain ionic species, such as $COCl^+$ or CO^{2+} cations and $AlCl_4^-$ anions, and the solid complexes obtainable from these solutions were also thought to be ionic. Subsequently, Huston[39] has shown that the exchange rate of radioactive chlorine for very dilute (less than 2 equivalent fraction per cent) aluminium chloride solutions in phosgene is very slow, exchange half-lives varying between 12 and 60 hours at $0°C$. This slow exchange would be extremely improbable if ionic species were involved. Huston also showed the exchange to be homogeneous. In a later paper, however[40], he modified this view to allow for the appearance of ions at

higher concentrations, the exact concentration at which ions first appear in the solution being dependent on temperature. (Approximately 10 equivalent fraction per cent at $-21^\circ C$, 2 at $0^\circ C$ and 0.3 at $25^\circ C$).

More recently, Jones and Wood[41] and Christe[42] have shown that only the 1:1 complex exists at ambient temperatures, this being a white, easily dissociated solid, melting point $25^\circ C$. Both sets of workers overcame extreme experimental difficulties caused by the reactivity of the complex to obtain its infra-red spectrum. Although there are some wide discrepancies between the two sets of band assignments, both papers agree on the dative covalent nature of the complex, with co-ordination through the oxygen to aluminium.
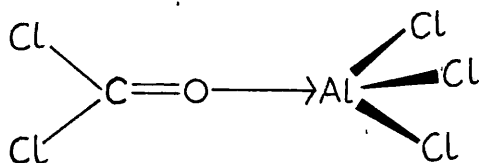
Christe confirmed the 1:1 aluminium chloride/phosgene complex by measurement of vapour pressure - composition curves at $0^\circ C$ and $25^\circ C$, when both a negative deviation from Raoult's Law and a sharp break at a 1:1 mole ratio were found. However, with boron trichloride/carbonyl chloride, he found a positive

deviation from Raoult's Law, and no evidence for a complex.
This is rather surprising, since boron trichloride is generally
accepted to be a stronger Lewis acid than aluminium chloride[43,44].

Literature data on systems involving bromide is very sparse.
A. von Bartal[45] claimed that aluminium bromide reacted with
excess phosgene according to the equation

$$AlBr_3 + 3COCl_2 = AlCl_3 + 3COClBr.$$
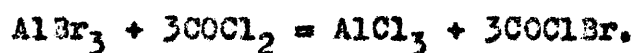
With the aluminium bromide in excess, however, at $100^{\circ}C$
aluminium dichlorobromide, $AlBrCl_2$, was supposed to be formed
as a brick-red solid, melting at $142-143^{\circ}C$. Identification of
this substance was based on analysis. The red colour seems
rather surprising in view of the fact that both aluminium
chloride and aluminium bromide are white. In a much later
paper[46], Corbett and Gregory repeated the experiment, and found
that the red colour was due to free bromine. Also, the
crystals obtained resembled an annealed mixture of aluminium
chloride and aluminium bromide rather than any mixed halide
phase involving $AlBrCl_2$; no analytical data were given.
Aluminium dichlorobromide is known, however, from the reaction
of hydrogen chloride on aluminium bromide[46,47].

The objects of the present work were:-
(i) In view of the failure of Christe[42] to find a complex
between boron trichloride and carbonyl chloride, to investigate
the system boron tribromide/carbonyl bromide. Boron tribromide

is a better Lewis acid than boron trichloride due to the smaller degree of π-bonding involved in the molecule, leading to a smaller reorganisation energy for the transition $B\,sp^2 \longrightarrow B\,sp^3$ required on complexing[48,49,50]. Carbonyl bromide, despite being thermodynamically much less stable than phosgene with respect to the dissociation

$$COX_2(l) \rightleftharpoons CO(g) + X_2(l) \text{ or } (g) \text{ [See Part 3]}$$

might be expected to behave as a better donor because of the lower electronegativity of bromine compared with chlorine[51]. There is the added advantage that possible halogen exchange would be unimportant. Techniques employed were infra-red spectroscopy of gaseous mixtures and solid mixtures, and the ^{11}B magnetic resonance of liquid mixtures.

(ii) To re-investigate the reaction between aluminium bromide and phosgene, and also the other combinations:

> Aluminium chloride/carbonyl bromide
>
> Aluminium bromide/carbonyl bromide
>
> Aluminium iodide/carbonyl chloride

with a view not only to establishing the products of exchange reactions, but also determining any complex formation, both at room temperature and below.

Techniques employed were:-

(a) Mixing the two components, both at room temperature and low temperatures, pumping off volatile products, then weighing and analysing the residues.

(b) Infra-red spectroscopy of the vapours from the mixtures.

In both (i) and (ii), infra-red and Raman spectra of both solutions and residues would have been invaluable. However, sufficiently inert materials suitable for fabricating infra-red cells were not available (compare reference 41, where the complex aluminium chloride/carbonyl chloride is stated to attack sodium chloride, potassium bromide, silver chloride and polythene). Infra-red spectra of the residues yielded only bands too broad and too weak to be assigned. Measurement of Raman spectra was attempted, but each time strong fluorescence obscured any bands. This was possibly due to bromine being present in very low concentrations, since it is well known[52] that minute quantities of coloured impurities can cause strong fluorescence.

EXPERIMENTAL

Apparatus and Procedure

All the compounds were handled on a modification of the
grease-free vacuum line described in Part One (p. 27)
(diagram 10). Volatile compounds were stored in the grease-
free containers, A and B, from which samples could be distilled
into the respective U-tubes and then into the mixing tube, C.
This mixing tube was fitted with a greaseless tap and attached
to the line via a greaseless joint, so that it could be readily
detached and weighed. Having obtained the required mixture,
one of the storage containers could then be replaced by an
infra-red cell or N.M.R. tube as required. The relatively
involatile, solid, aluminium halides were loaded into the
mixing tube in a dry-box, and the mixing tube then attached to
the line and evacuated.

For infra-red gas phase spectra, a cell specially designed
and constructed in the department was used (diagram 11). The
cell, path-length 10 cm, was fitted with potassium bromide
windows, held on and sealed by Viton 'O-rings' and metal screw
caps. It was also fitted with a "Uniform" greaseless tap
(Glass Precision Engineering Co. Ltd.), and with an 'O-ring'
joint for attachment to the vacuum line. It was capable of
holding a vacuum of $\underline{ca}$. 10^{-4} torr. For filling with the vapour

VACUUM SYSTEM FOR CARBONYL HALIDES

GROUP THREE HALIDES

DIAGRAM 10

To Pump

Greaseless Tap

A

B

C

54
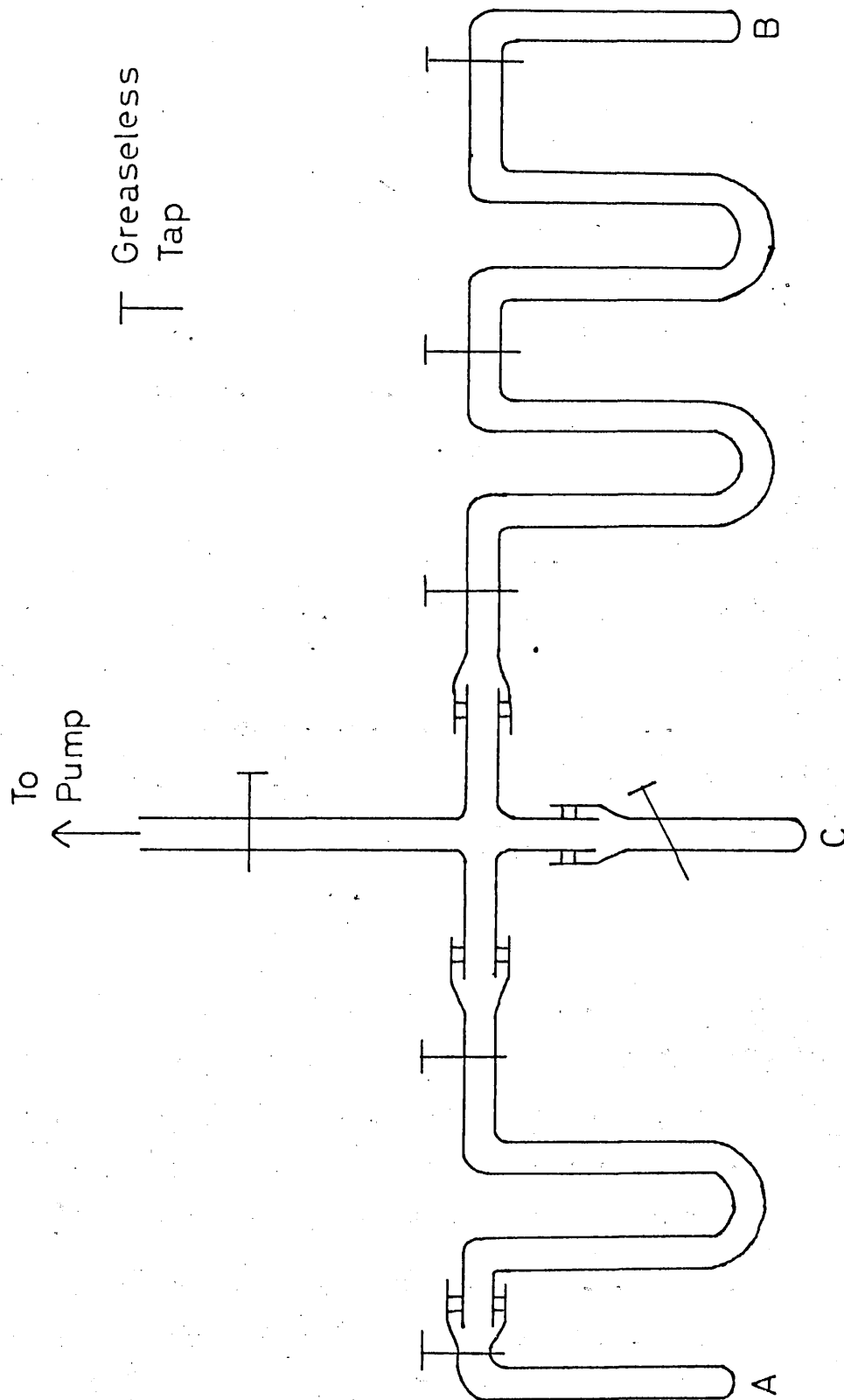
DIAGRAM 11   INFRA—RED GAS CELL

Polypropylene Cap

P.T.F.E. Plunger

Metal Screw Cap

Metal Screw Thread

K Br Plate

Cork Washer

Viton Rubber 'O' Ring
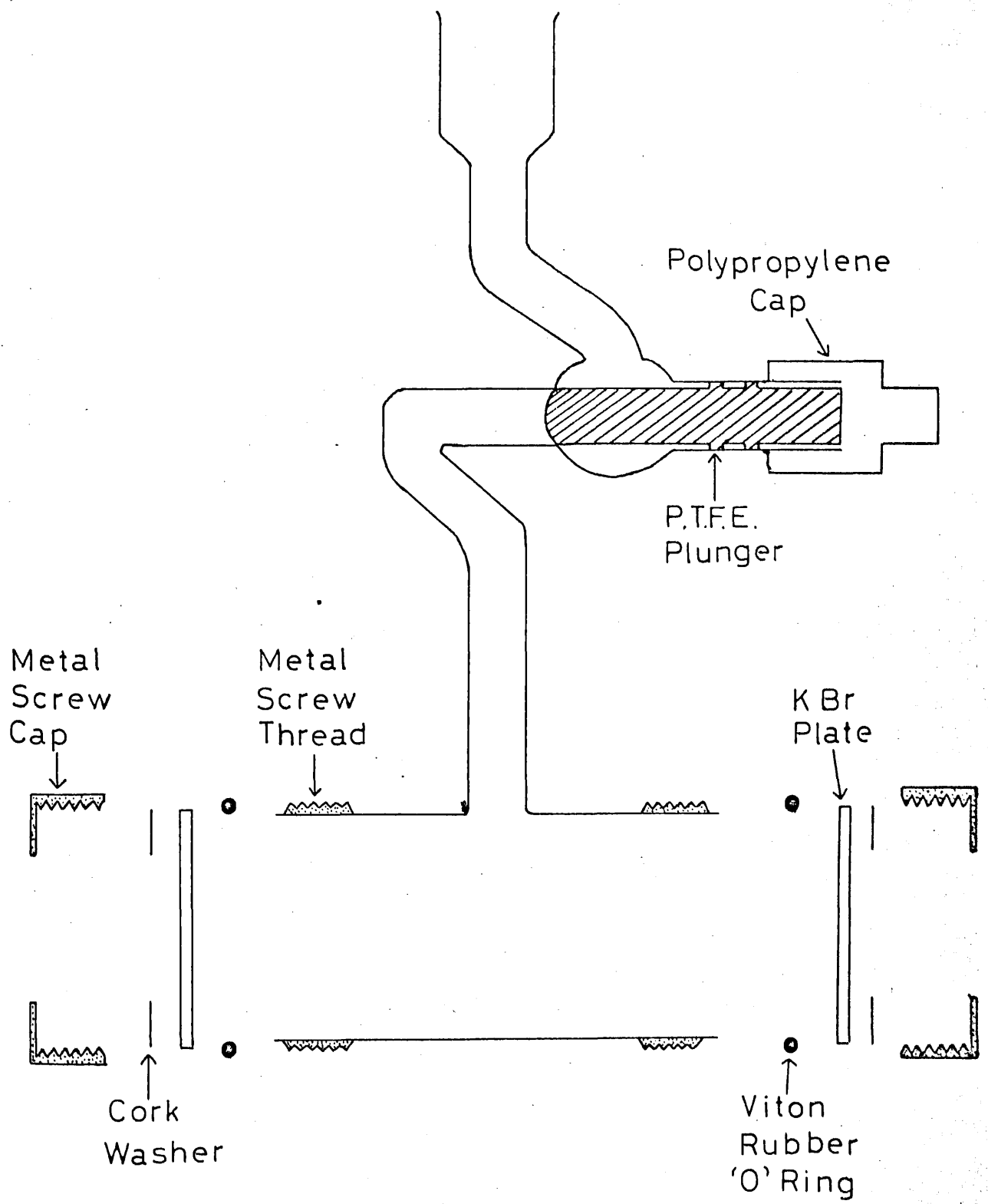
from a reaction mixture, the cell and mixing vessel were both evacuated, and then closed to the pump. The taps connecting the two were opened, and the system allowed to come to equilibrium. After shutting the taps and pumping away excess vapour, the cell could usually be removed from the line simply by sliding the joint apart, despite the vacuum inside. In a few instances, it was necessary to shrink the 'O-rings' of the joint, using a little liquid nitrogen, in order to pull it apart. To run the spectrum of a gaseous mixture of boron tribromide and carbonyl bromide, the cell was attached to the line in place of the mixing vessel. Each of the components, stored in vessels A and B, was distilled into its respective U-trap, where they were thermostated such that the two vapour pressures were nearly identical, and of a suitable value to obtain reasonable peak heights in the spectra. The boron tribromide was kept at room temperature (approximately $20^{\circ}C$) and the carbonyl bromide at approximately $-5^{\circ}C$ (ice/salt bath), where both have vapour pressures in the region 50 torr[4,53]. The vapours were then allowed to mix, and the cell filled.

The spectrum of a solid boron tribromide/carbonyl bromide mixture was obtained by using the cold cell shown in diagram 12. A 1:1 mixture of the vapours, prepared as described above, was sprayed through the fine nozzle on to the caesium iodide plate.

DIAGRAM 12   LOW TEMPERATURE
INFRA—RED CELL

To Vacuum Line

To Vacuum
Line & Sample

Copper
Holder

K Br
Plate

Cs I
Plate

57
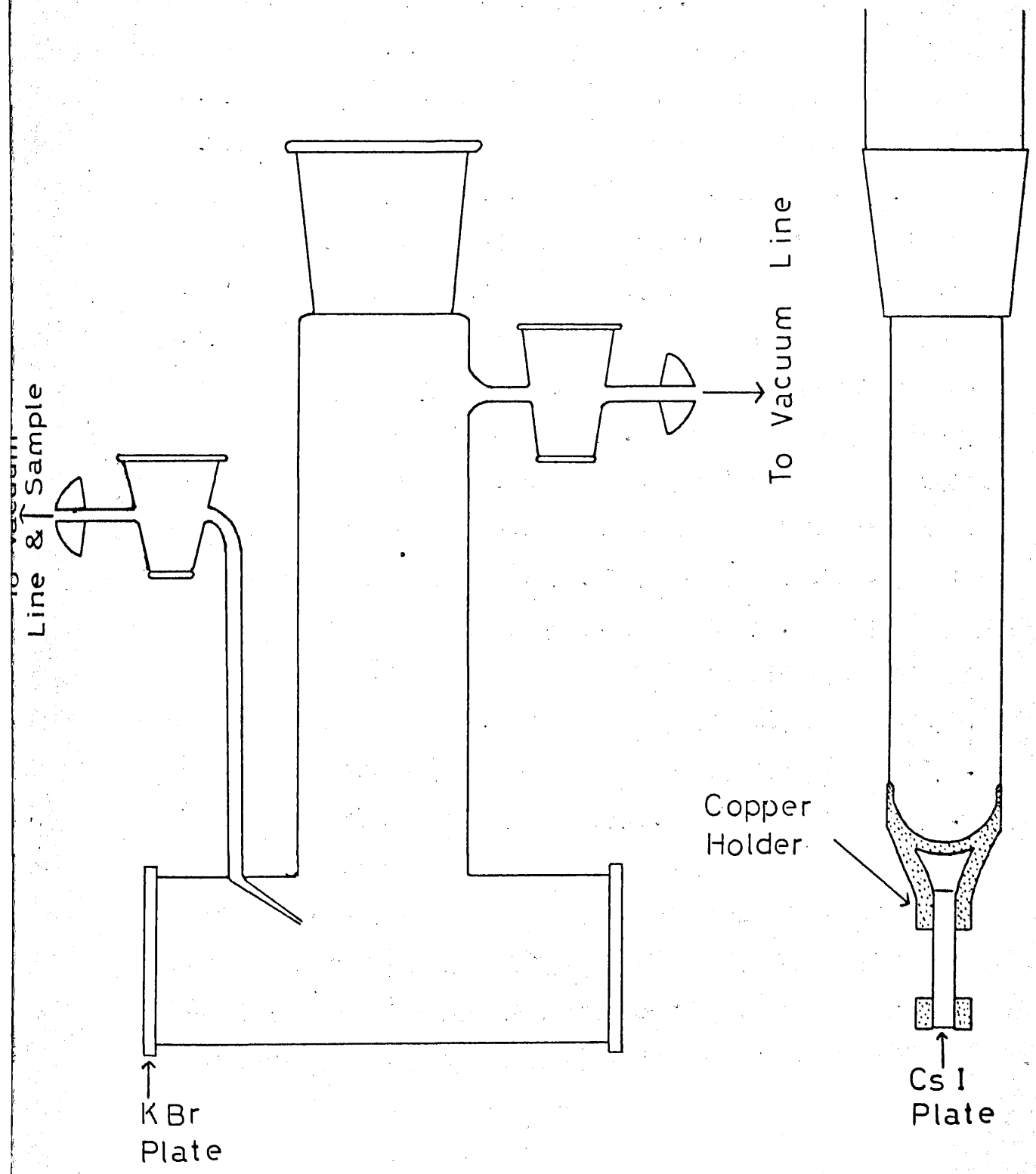
Caesium iodide was used due to its superior resistance to thermally-induced strain compared with most common window materials. The plate was sited in a copper holder cooled by liquid nitrogen. After spraying on the mixture, the plate could be rotated by means of the greased joint at the top of the apparatus so as to align it with the potassium bromide windows. Care had to be taken that the greased joint did not sieze due to the extreme cold. Best mobility was obtained using Apiezon N grease (May and Baker). Another problem encountered in humid weather was that of water and carbon dioxide condensing on the outside of the potassium bromide plates due to the cooling of the apparatus, and spurious bands were obtained in the spectra at approximately 3600 cm^{-1} and 1600 cm^{-1}, (water) and 665 cm^{-1} (carbon dioxide). The one doubt about the principle of the method might be that, for weak complexes where there is interaction in the solid but not the gas phase, spraying a gaseous mixture on to a cold plate gives not a mixed crystal, but a mixture of the individual crystals. However, using a similar method for bromine/benzene, Person[54] showed that only the mixed crystal was formed, and complexing was observed.

All infra-red spectra described above were run on a Perkin-Elmer 337 instrument, giving a resolution of approximately ± 5 cm.$^{-1}$.

Infra-red spectra of the residues from aluminium halide/
carbonyl halide reactions were attempted as nujol mulls and
dry powders, between potassium bromide plates. These spectra
were run on a Perkin-Elmer 325 instrument. However, the bands
obtained were always too broad and weak to be of use in
identifying the residues.

Raman spectra of solutions and solids were attempted on
both Cary 81 (helium/neon laser, 6328$\overset{o}{A}$ exciting line) and Spex
Ramalog (ionised argon laser, 5147$\overset{o}{A}$ exciting line) instruments,
but all samples fluoresced so strongly as to completely obscure
any bands. The samples were made up by filling thick-walled
capillary tubes (with flattened bases of thinner glass) in a
dry-box situated in a fume cupboard, then freezing, and sealing
off the tubes.

^{11}B nuclear magnetic resonance for boron tribromide/
carbonyl bromide and pure boron tribromide was carried out on a
Perkin-Elmer R10 instrument (60 MH_z). Two N.M.R. tubes, each
containing a sealed capillary of boron trifluoride etherate,
$BF_3.OEt_2$, as external reference, and fitted with a greaseless
joint, were attached to the vacuum line and filled respectively
with pure boron tribromide and an approximately 1:1 mixture of
boron tribromide/carbonyl bromide. They were then sealed, and
the spectra run. Shifts were measured accurately to $\pm$ 3 p.p.m.

For studying the reactions of aluminium halides and carbonyl halides, the mixing vessel was evacuated, weighed, loaded with aluminium halide in a dry-box, then re-evacuated and re-weighed. Carbonyl halide was distilled in, and the mixing vessel re-weighed. The system was then thermostated if required. After pumping off carbonyl halide at low temperature, usually $-45 \pm 1^\circ C$, (chlorobenzene slush bath), the mixing vessel was re-weighed to see if there was any addition in weight corresponding to complex formation. Comparison with the method of preparation[39] and dissociation pressures[42] quoted for aluminium chloride/carbonyl chloride showed the unlikelihood of decomposing any complex formed by pumping away excess carbonyl halide at $-45^\circ C$. After pumping to dryness at room temperature the residue was weighed, hydrolysed, and analysed as follows:-

Excess sodium hydroxide solution (concentration not critical) was placed in the mixing vessel above the tap, and the vessel stoppered. The tap was slowly opened to allow gradual hydrolysis of the residue. After shaking to dissolve the residue completely, the hydrolysate was made up to a standard volume in slightly acid solution (HNO_3). The addition of acid was to prevent the slow precipitation of various aluminium/hydroxide species which occurs in alkaline solution on standing, and which are very difficult to redissolve. The hydrolysis

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itself had to be carried out in alkaline medium because
aluminium bromide, unlike aluminium chloride, hydrolyses only
extremely slowly at pH $\ll 7$ [55]. Total halide concentration was
determined by Volhard's method [56], involving the precipitation
of silver halide from nitric acid solution with excess 0.1N
silver nitrate, filtering, and back-titrating the excess
silver nitrate with 0.1N ammonium thiocyanate, using ferric
indicator. Chloride was determined [57] by first removing
bromide by oxidation to bromine with potassium iodate in acid
solution, followed by boiling. Excess iodate was removed by
reduction with phosphorous acid, H_3PO_3, and boiling off the
iodine so formed. The chloride solution remaining was then
titrated by Volhard's method as above, the bromide present
being obtained by difference. Aluminium was determined gravi-
metrically by precipitation as the 8-hydroxyquinolate
("oxinate"), $Al(C_9H_6ON)_3$, in ammonium acetate buffer (reference
56, p. 388 and 516). The precipitate was collected in a
sintered glass crucible (porosity No. 4), washed, dried at $120^\circ C$,
and weighed.

Chemicals

Carbonyl bromide was prepared according to the method of
Schumacher and Lenher [53], by the reaction of carbon tetrabromide
with concentrated sulphuric acid (specific gravity 1.83) at
150-170°C. The carbon tetrabromide was heated just to melting

in a dry, nitrogen-filled atmosphere, and the sulphuric acid
added dropwise from a funnel.   After all the sulphuric acid
had been added, the mixture was heated to 150-170°C, when all
the volatile products of the reaction distilled off, and were
condensed using a cold finger filled with an ice/salt mixture.
The distillate was collected in a flask cooled in a solid
carbon dioxide/acetone slush bath.   The dark-brown distillate
contained, apart from carbonyl bromide, considerable quantities
of free bromine, hydrogen bromide, and assorted sulphur
compounds.   The apparatus was open to the atmosphere via a
drying bottle (concentrated sulphuric acid) to allow for the
escape of carbon monoxide also formed in the reaction.

The bromine was removed by the very slow addition of
mercury while shaking and cooling the liquid.   [This process
must be carried out very carefully, since the large heat of
reaction between mercury and bromine can easily lead to
decomposition of the carbonyl bromide

$$COBr_2(l) \rightleftharpoons CO(g) + Br_2(l) + (g) \quad]$$
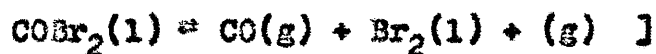
The mercuric bromide formed "tailed off" to give a coating on
the wall of the flask, while the liquid turned from dark brown
to pale yellow.

The carbonyl bromide was distilled off at atmospheric
pressure, the portion boiling between 61-65°C being retained.

The last traces of bromine were removed by the careful addition of small quantities of antimony powder, while cooling, and a further distillation at reduced pressure yielded colourless carbonyl bromide (boiling point at atmospheric pressure $64.5 \pm 0.5^{\circ}C$, literature value[53] $64-65^{\circ}C$). The yield for the preparation varied between 20-40% of theoretical based on the equation

$$CBr_4 + [O] \longrightarrow COBr_2 + Br_2 .$$
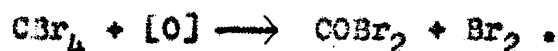
Carbonyl bromide is extremely poisonous, so all distillations were carried out in a well-ventilated fume cupboard, and the apparatus was open to the atmosphere only via a concentrated sulphuric acid washbottle (to exclude moisture) and a washbottle of concentrated alkali to decompose any carbonyl bromide vapour:-

$$2NaOH + COBr_2 \longrightarrow 2NaBr + CO_2 + H_2O$$
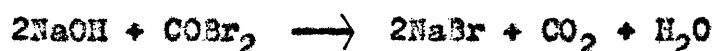
The carbonyl bromide was introduced into the vacuum line, degassed by repeated freezing and pumping, and stored in the dark at $-196^{\circ}C$ (liquid nitrogen). When a sample was required, it was fractionated through $-45^{\circ}C$ (chlorobenzene slush bath) to a trap at $-94^{\circ}C$ (toluene slush bath), at which temperature any hydrogen bromide impurity would be pumped away (vapour pressure[4] approximately 500 torr).

The purity of the carbonyl bromide was tested by
hydrolysing a sample with alkali, as described for aluminium
halides above, and titrating by Volhard's method.   A typical
result, using a 0.339g sample made up to 200 ml solution was

      Br (found)   84.6% by mass

      Br (calculated) 85.1% by mass

To test for the presence of free bromine, potassium iodide
was added to a slightly acid post-hydrolysis solution,
followed by a drop of starch solution.   The absence of any
immediate blue colour due to starch-iodine complex showed the
iodine concentration to be less than $2 \times 10^{-5} M$ [58], corresponding
to a bromine content in carbonyl bromide of less than one half
of one per cent.

Commercial carbonyl chloride (Matheson Co. Ltd.), supplied
in a cylinder under pressure, with stated purity 99.0% minimum,
was further purified by fractionation as for carbonyl bromide.
The cylinder was connected to the vacuum line by a length of
reinforced polythene tubing, the joint either end being made
vacuum tight by application of "Torrseal" resin (Varian Ltd).

Boron tribromide was purified as described previously
(p. 29).

Commercial aluminium chloride and aluminium bromide
(B.D.H. Ltd.), with minimum stated purities 98% and 99%
respectively, were vacuum sublimed several times each, the
first few times from a mixture with finely-divided aluminium
powder to remove water and free halogen.   A minimum of
heating had to be used for these sublimations, because on
heating at low pressures, the reaction

$$2Al(s) + AlX_3(s) \longrightarrow 3AlX(g)$$
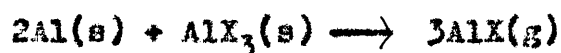
tends to occur[59].   On condensing, the monohalide dispro-
portionates to the trihalide and aluminium again, resulting
in a transfer of aluminium metal to the final product.

After sublimation, both trihalides were white, crystalline
solids, though the tribromide darkened slightly after several
months even though stored in the dark.   The purities were
tested by alkaline hydrolysis followed by halide and aluminium
determination as described above.   The results were

$AlCl_3$ Cl(found) 79.1% by mass   Al(found) 20.3% by mass
      Cl(calc.) 79.7% by mass   Al(calc.) 20.3% by mass

$AlBr_3$ Br(found) 89.8% by mass   Al(found) 10.2% by mass
      Br(calc.) 89.9% by mass   Al(calc.) 10.1% by mass

Attempts to purify commercial aluminium iodide (Alfa
Inorganics; no stated purity) by sublimation resulted only in

further decomposition to aluminium and iodine. Likewise,
preparation from the elements according to the method of
Watt and Hall[60] resulted only in discoloured product.
Probably this was due to the difficulty in the method, which
involved subliming iodine through heated aluminium granules,
of packing the aluminium extremely tightly. Only one-third
of the quoted weight of aluminium per unit volume of apparatus
could be achieved. Therefore, the commercial product,
supplied as a pink powder compared with the white colour of
pure aluminium iodide, was used directly, since analysis
showed the purity to be better than 99%, despite the dis-
colouration.

AlI_3 I(found) 93.2% by mass   Al(found) 7.0% by mass
        I(calc.) 93.4% by mass   Al(calc.) 6.6% by mass

RESULTS

Boron Tribromide + Carbonyl Bromide

On mixing boron tribromide and carbonyl bromide, a colourless solution resulted, which turned very slowly brown on standing in the light for several hours, due to decomposition of carbonyl bromide. The rate of appearance of bromine colour was about the same as for pure carbonyl bromide under the same conditions.

The gas phase spectra of boron tribromide, carbonyl bromide, and an approximate 1:1 gaseous mixture of the two are shown in diagrams 13, 14 and 15 respectively, and the frequencies listed in table 9.

All frequencies are $\pm$ 5 cm^{-1}.

The spectra of boron tribromide and carbonyl bromide agree very well with published spectra[61,62], except for the presence of a PQR band at 1362 cm^{-1} in the carbonyl bromide spectrum. This is almost certainly due to the extremely strong ν_3 fundamental (1362 cm^{-1}) of sulphur dioxide[63], present as an impurity from the preparation. The intensity of this band indicates that the sulphur dioxide was present in only small concentrations, and indeed after the first few samples the band disappeared (compare, for example, with the carbonyl bromide/ boron tribromide spectrum, diagram 15).

TABLE 9

GAS PHASE INFRA-RED FREQUENCIES OF BORON TRIBROMIDE/CARBONYL BROMIDE

ASSIGNMENT (REF. 61)	CARBONYL BROMIDE cm^{-1}	CARBONYL BROMIDE/ BORON TRI- BROMIDE	BORON TRI- BROMIDE cm^{-1}	ASSIGNMENT (REF. 62)
$2\nu_2$	3633 m	3632 w		
ν_2	1822 s	1822 s		
$3\nu_5 + \nu_4$	1790 m	1795 m		
		1715 w	1715 m	$2\nu_3(^{10}B)$
		1639 m	1641 m	$2\nu_3(^{11}B)$
$2\nu_4$	1510 m	–		
$2\nu_5 + \nu_4$	1480 m	–		
		1375 w	1373 m	$2\nu_1 + \nu_3(^{11}B)$
SO_2 impurity	1362 s	–		
$2\nu_1 + \nu_5$	1214 w	–		
$\nu_4 + \nu_1$	1160 m	–		
		1132 m	1132 m	$\nu_1 + \nu_3(^{10}B)$
		1093 m	1093 s	$\nu_1 + \nu_3(^{11}B)$
$2\nu_6$	1018 w	–		
		–	1000 w	$\nu_3 + \nu_4(^{10}B)$
		967 m	967 m	$\nu_3 + \nu_4(^{11}B)$
$\nu_3 + \nu_4$	918 w	–		
		910 w	911 m	$2\nu_1 + \nu_2(^{11}B)$
		855 vs	854 vs	$\nu_3 \ (^{10}B)$
		818 vs	815 vs	$\nu_3 \ (^{11}B)$
$\nu_1 + \nu_5$	786 vs	784 vs		
ν_4	741 vs	742 vs		
		575 w	574 m	$\nu_3 - \nu_1(^{10}B)$
$\nu_4 - \nu_3$	560 w	–		
		540 m	539 m	$\nu_3 - \nu_1(^{11}B)$
ν_6	512 m	512 w		
ν_1	427 m	423 m		

INFRA-RED SPECTRUM OF BORON TRIBROMIDE (GAS)

DIAGRAM 13

TRANSMITTANCE %

WAVENUMBER CM⁻¹

69

DIAGRAM 14   INFRA-RED SPECTRUM OF CARBONYL BROMIDE (GAS)
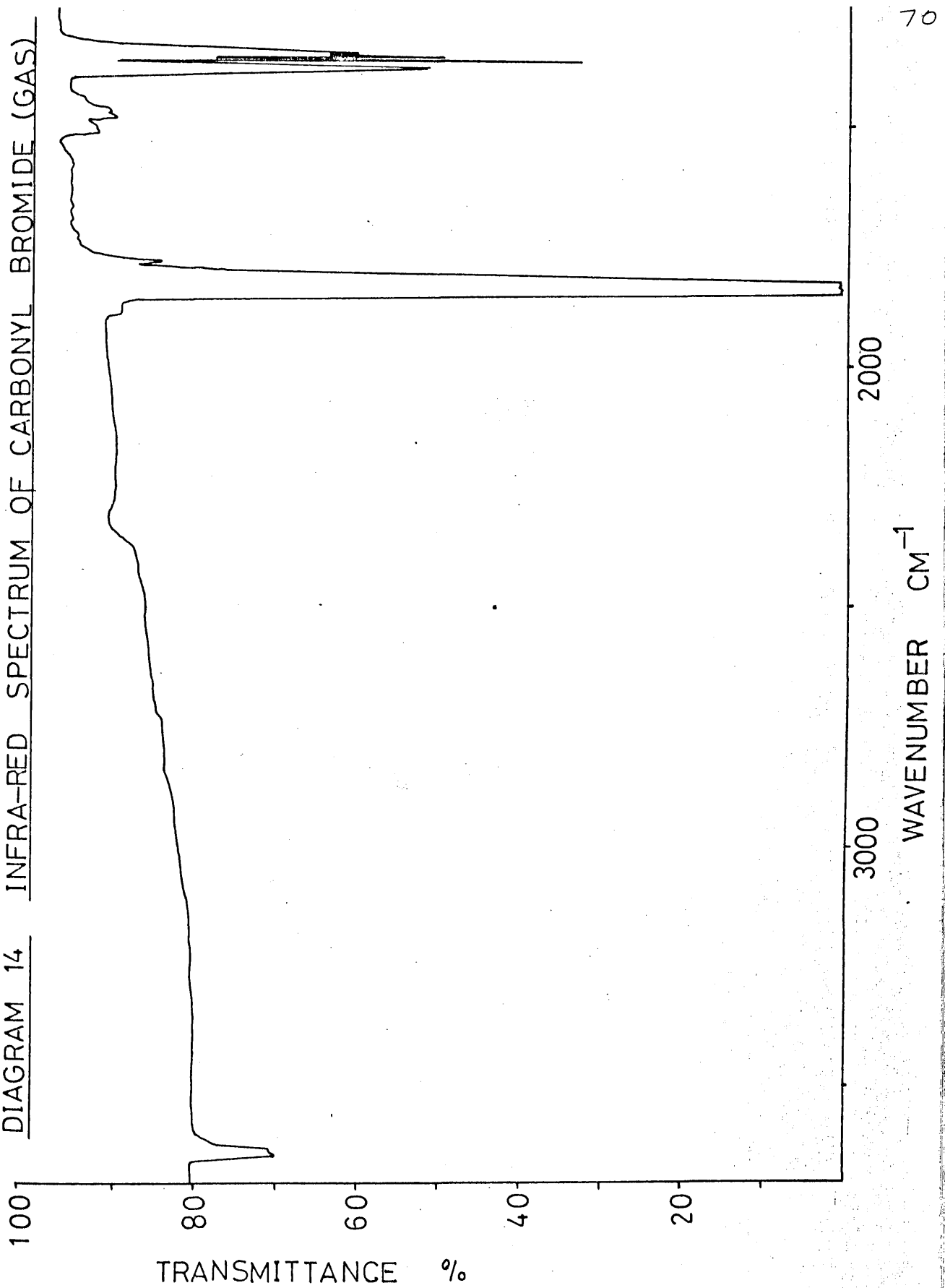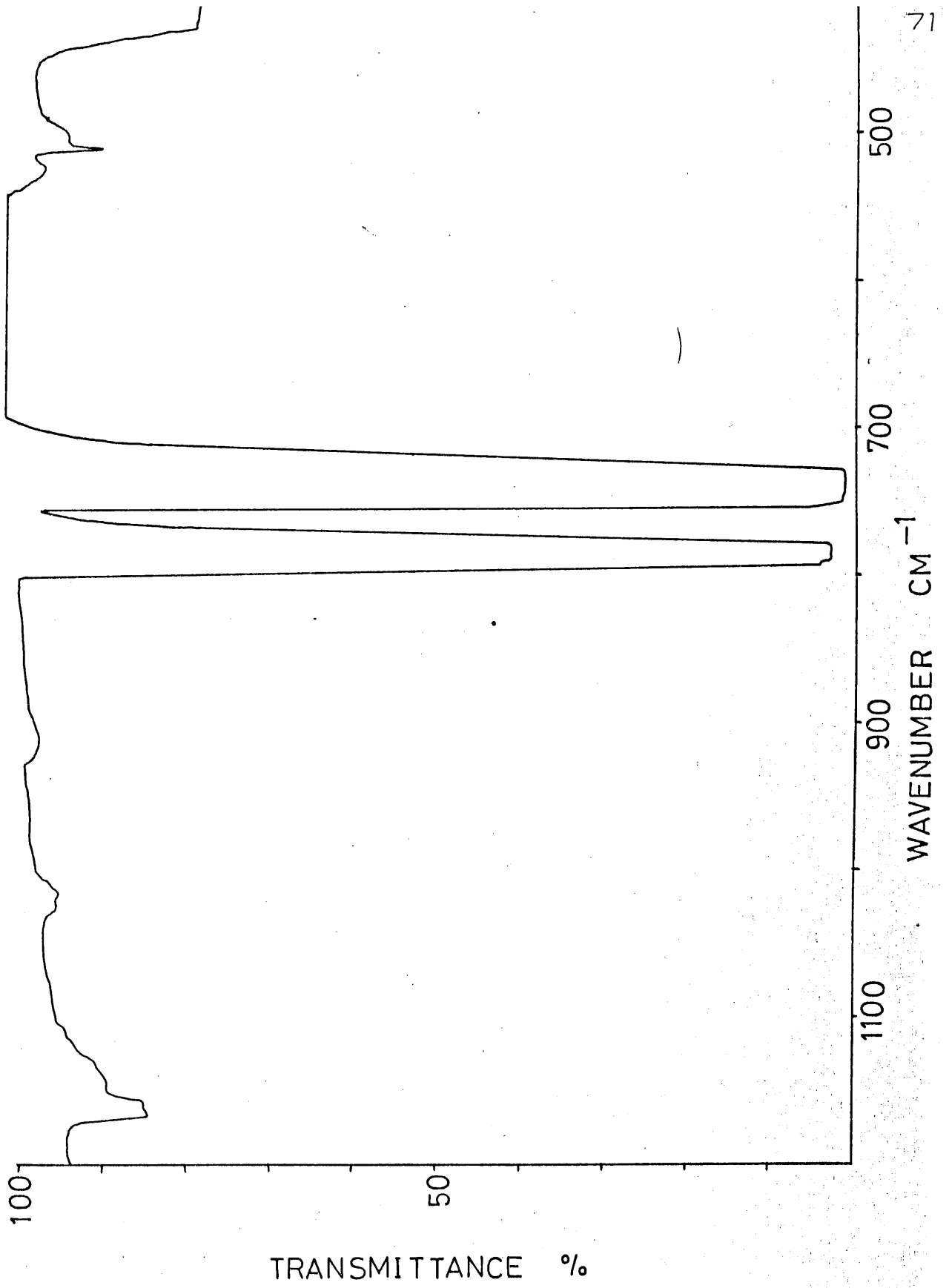
TRANSMITTANCE %

WAVENUMBER CM^{-1}

70

DIAGRAM 14 (CONT)

TRANSMITTANCE %

WAVENUMBER CM^{-1}

71

GAS PHASE
INFRA-RED SPECTRUM OF CARBONYL BROMIDE / BORON TRIBROMIDE

DIAGRAM 15

72

DIAGRAM 15 (CONT)

TRANSMITTANCE %

WAVENUMBER CM^{-1}

73
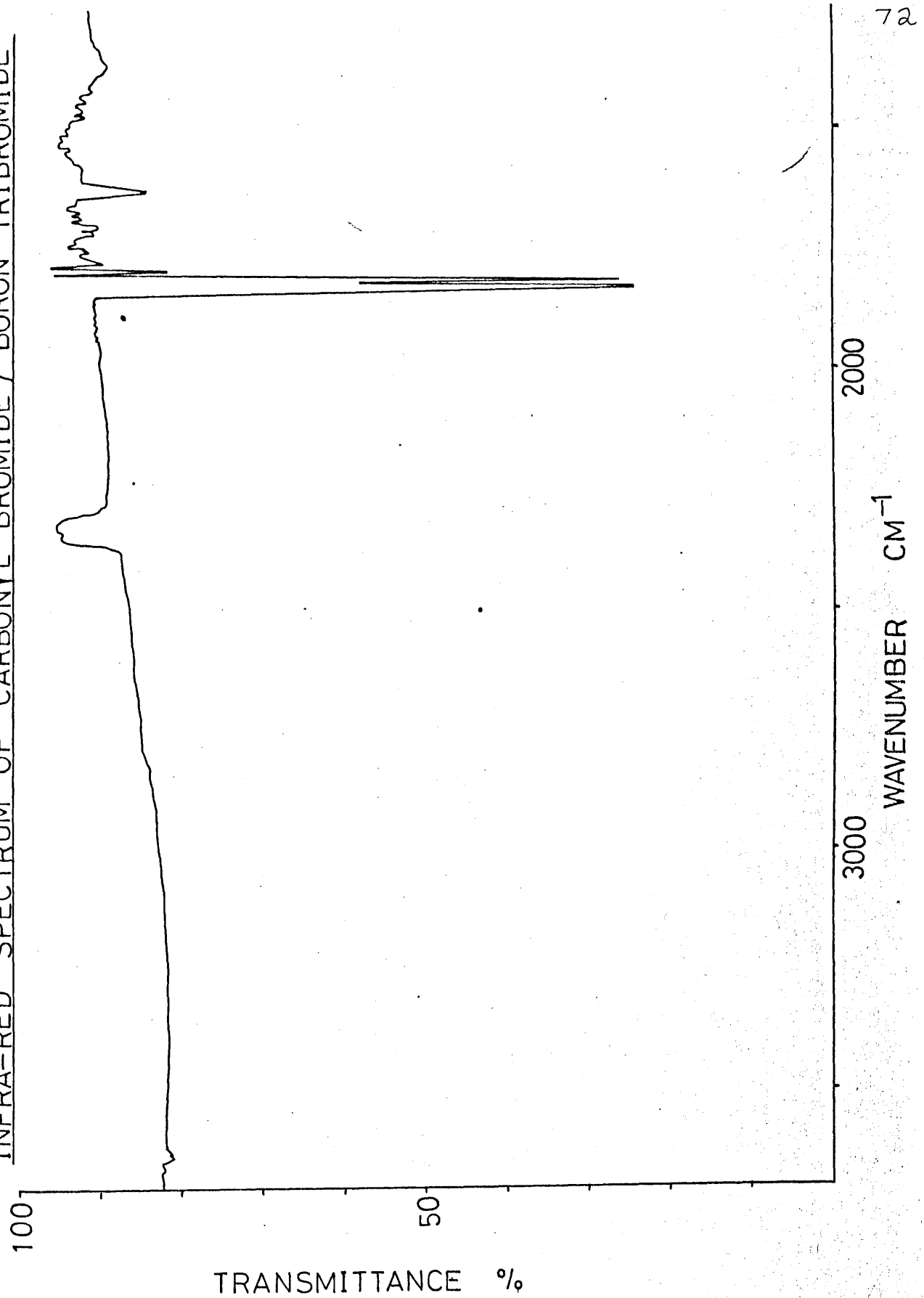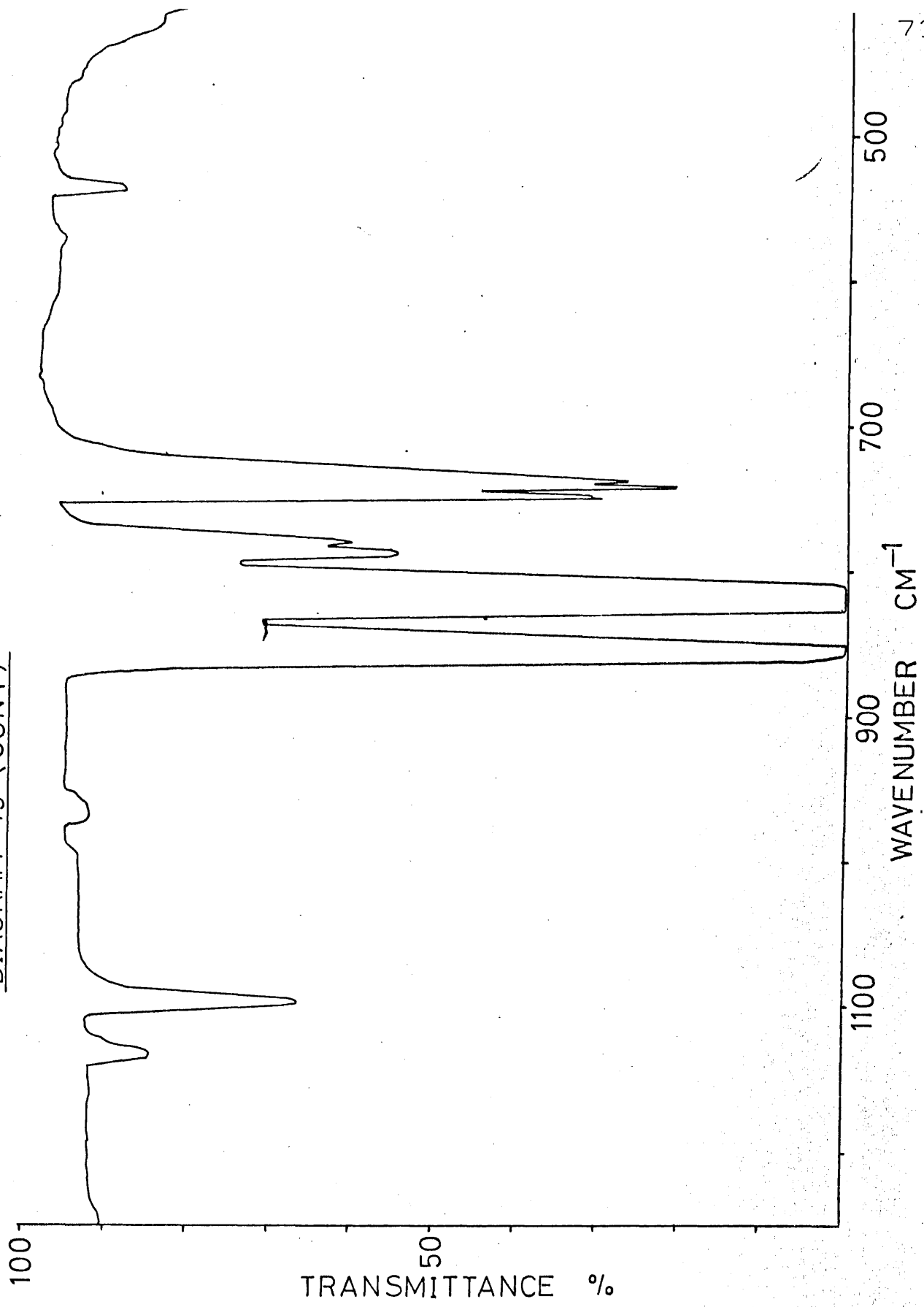
The spectrum of the 1:1 mixture is clearly a super-imposition of the two component spectra, whereas if there was any association in the gas phase, shifts or changes in relative intensity would be expected in some of the bands, accompanied possibly by new bands attributable to a B — O bond. Compare, for example, with aluminium chloride/carbonyl chloride, where a band assigned to a shifted C=O stretch appeared in the region 1600-1700 cm^{-1} [41,42].

Similar conclusions are reached from consideration of the spectra of the solids (diagrams 16, 17, 18; table 10). Although many of the bands show temperature shifts relative to the gas phase spectra, there are no shifts in the 1:1 mixture relative to the pure components. This strongly suggests that no complex exists even at low temperatures (less than $-100^{\circ}C$).

The ^{11}B nuclear magnetic resonance spectra again lend no support to the possibility of association. Samples of pure boron tribromide and 1:1 boron tribromide/carbonyl bromide both gave low-field shifts of 39 ± 3 p.p.m. relative to boron tri-fluoride etherate. No corrections for changes in bulk magnetic susceptibility have been attempted, since these would be insignificant relative to the limits of accuracy of the measurements.

TABLE 10
SOLID INFRA-RED FREQUENCIES FOR CARBONYL BROMIDE/BORON TRIBROMIDE

ASSIGNMENT	CARBONYL BROMIDE cm^{-1}	CARBONYL BROMIDE/ BORON TRI-BROMIDE	BORON TRI-BROMIDE cm^{-1}	ASSIGNMENT
$2\nu_2$	3570 w	—		
ν_2	1790 s	1792 s		
		1685 m	1688 m	$2\nu_3(^{10}B)$
		1600 m	1602 m	$2\nu_3(^{11}B)$
$2\nu_4$	1500 vw	—		
$2\nu_5 + \nu_4$	1430 m	1420 sh		
		1403 m	1403 m	$2\nu_1 + \nu_3(^{10}B)$
		1360 m	1365 m	$2\nu_1 + \nu_3(^{11}B)$
SO_2 impurity	1330 vw	—		
		1255 m	1252 m	?
$2\nu_1 + \nu_5$	1210 w	—		
$\nu_4 + \nu_1$	1140 m	—		
		1112 m	1108 m	$\nu_1 + \nu_3(^{10}B)$
		1070 s	1067 s	$\nu_1 + \nu_3(^{11}B)$
$2\nu_6$	1018 w	—		
		988 w	984 w	$\nu_3 + \nu_4(^{10}B)$
		945 m	940 m	$\nu_3 + \nu_4(^{11}B)$
		936 w	933 w	$2\nu_1 + \nu_2(^{10}B)$
		900 m	900 m	$2\nu_1 + \nu_2(^{11}B)$
$\nu_3 + \nu_4$	890 w	—		
		835 vs	860–760 vs	$\nu_3(^{10}B)$
		790 vs		$\nu_3(^{11}B)$
$\nu_1 + \nu_5$ ν_4	800–700 vs	720 vs		
		700 vs		
CO_2	660 m	665 m	670 m	CO_2
ν_6	506 m	506 m		
		480 w	485 w	$\nu_3 - \nu_1(^{10}B)$
		460 m	465 w	$\nu_3 - \nu_1(^{11}B)$
ν_1	420 w	425 sh		

DIAGRAM 16   INFRA-RED SPECTRUM OF BORON TRIBROMIDE (SOLID)

TRANSMITTANCE %

WAVENUMBER CM⁻¹

100   50

3000   2000

76

DIAGRAM 16 (CONT)

TRANSMITTANCE %

WAVENUMBER CM⁻¹

77
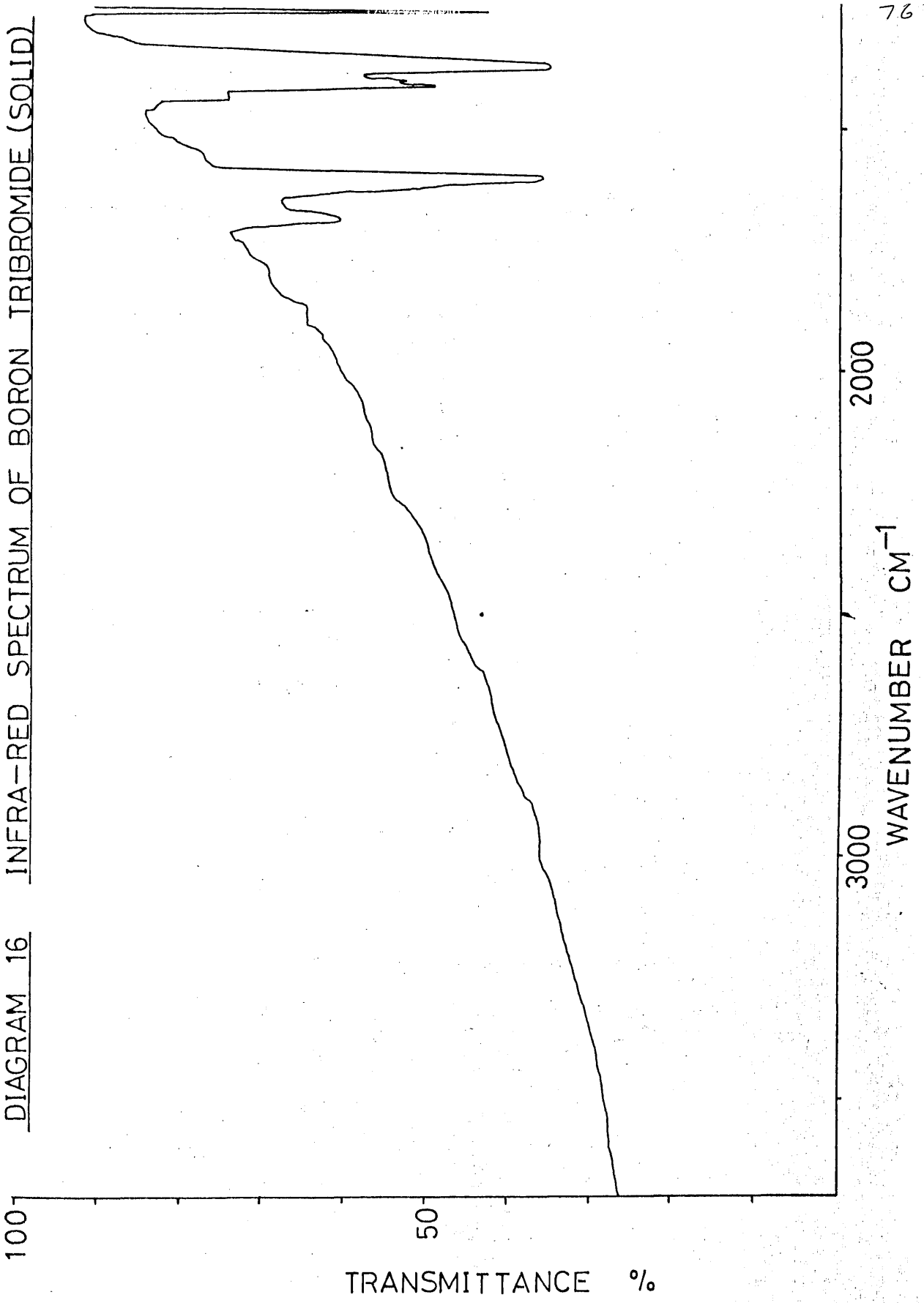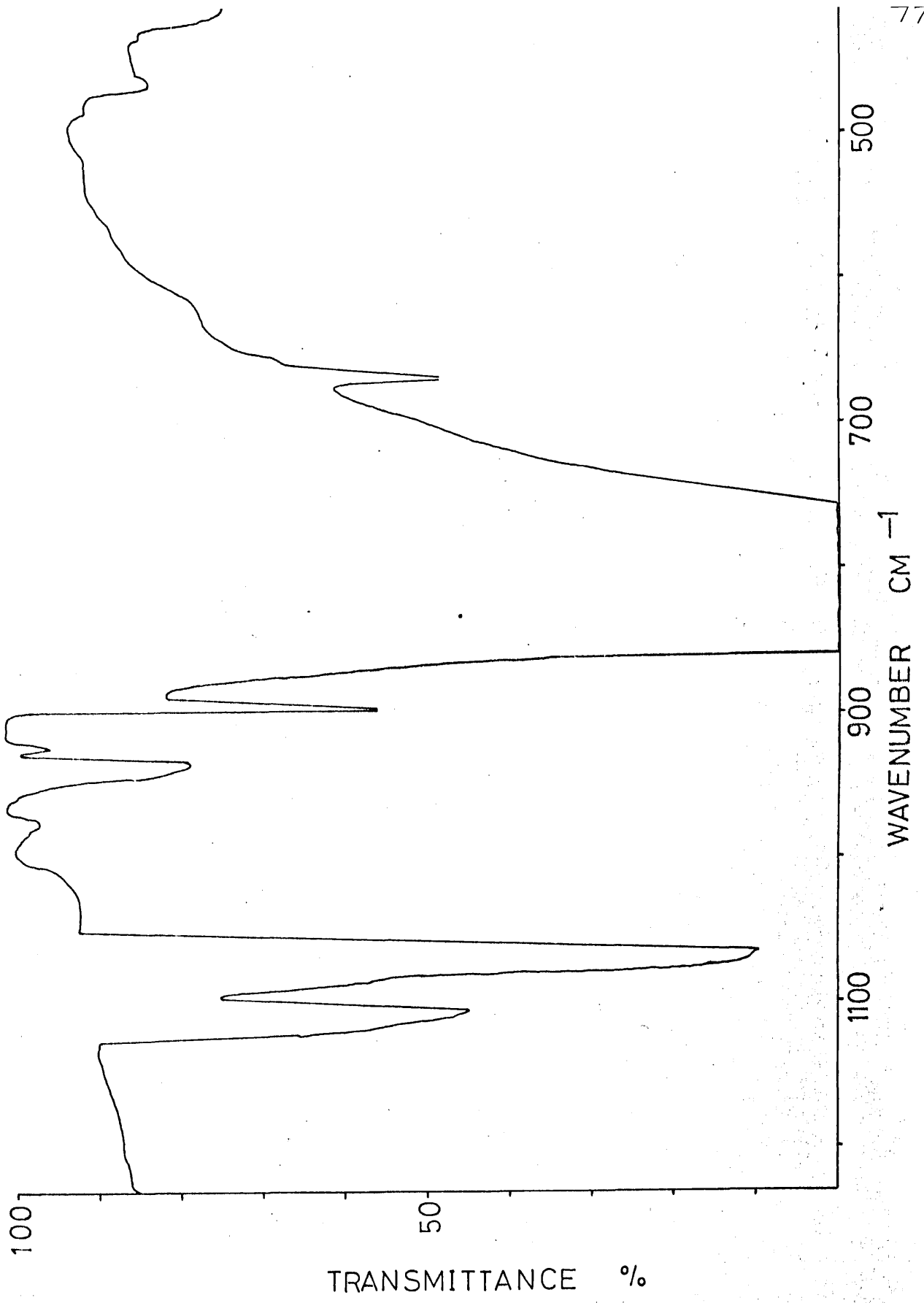
DIAGRAM 17   INFRA-RED SPECTRUM OF

CARBONYL BROMIDE (SOLID)

78

DIAGRAM 17 (CONT)

TRANSMITTANCE %

WAVENUMBER CM^{-1}

79
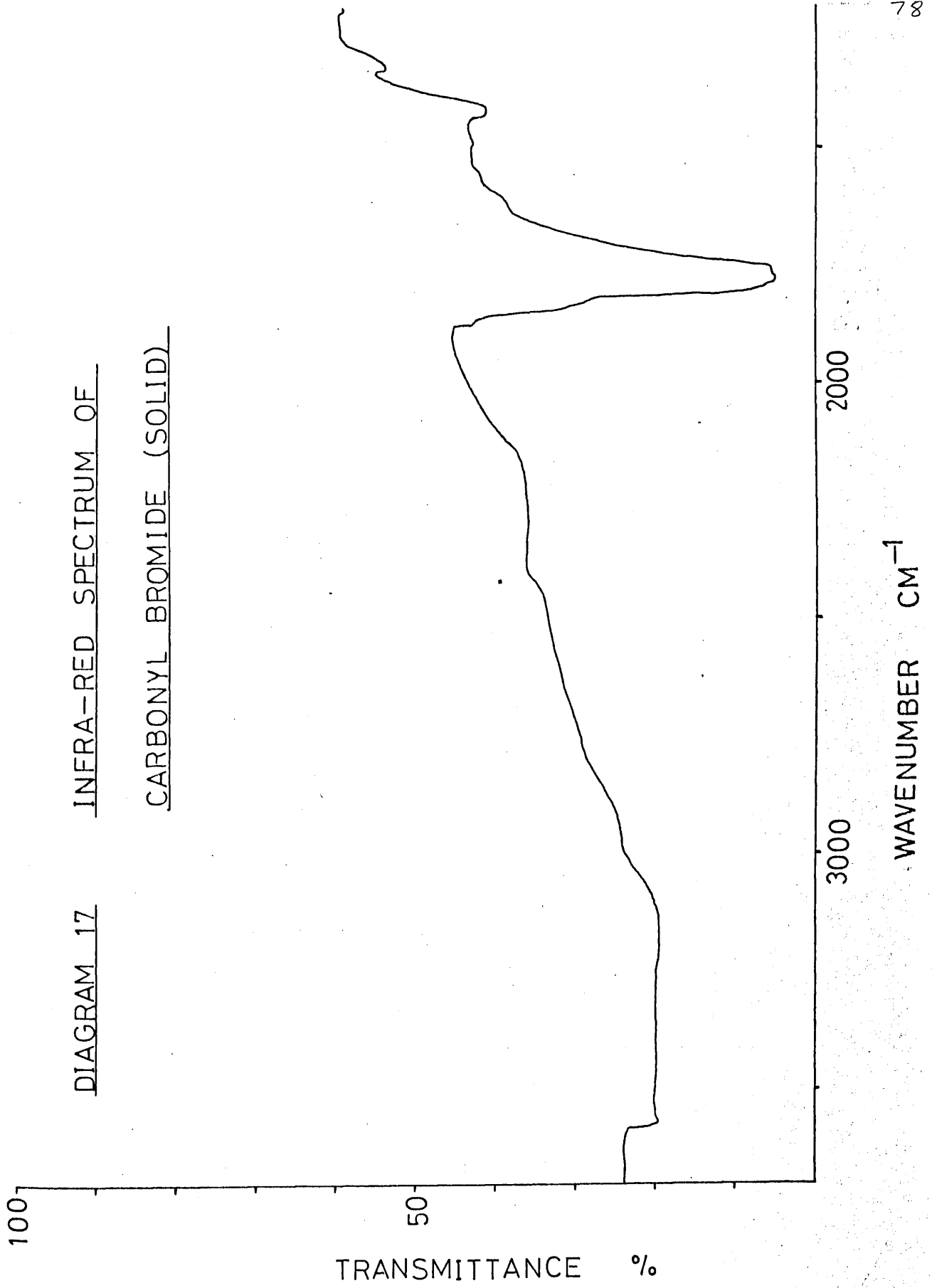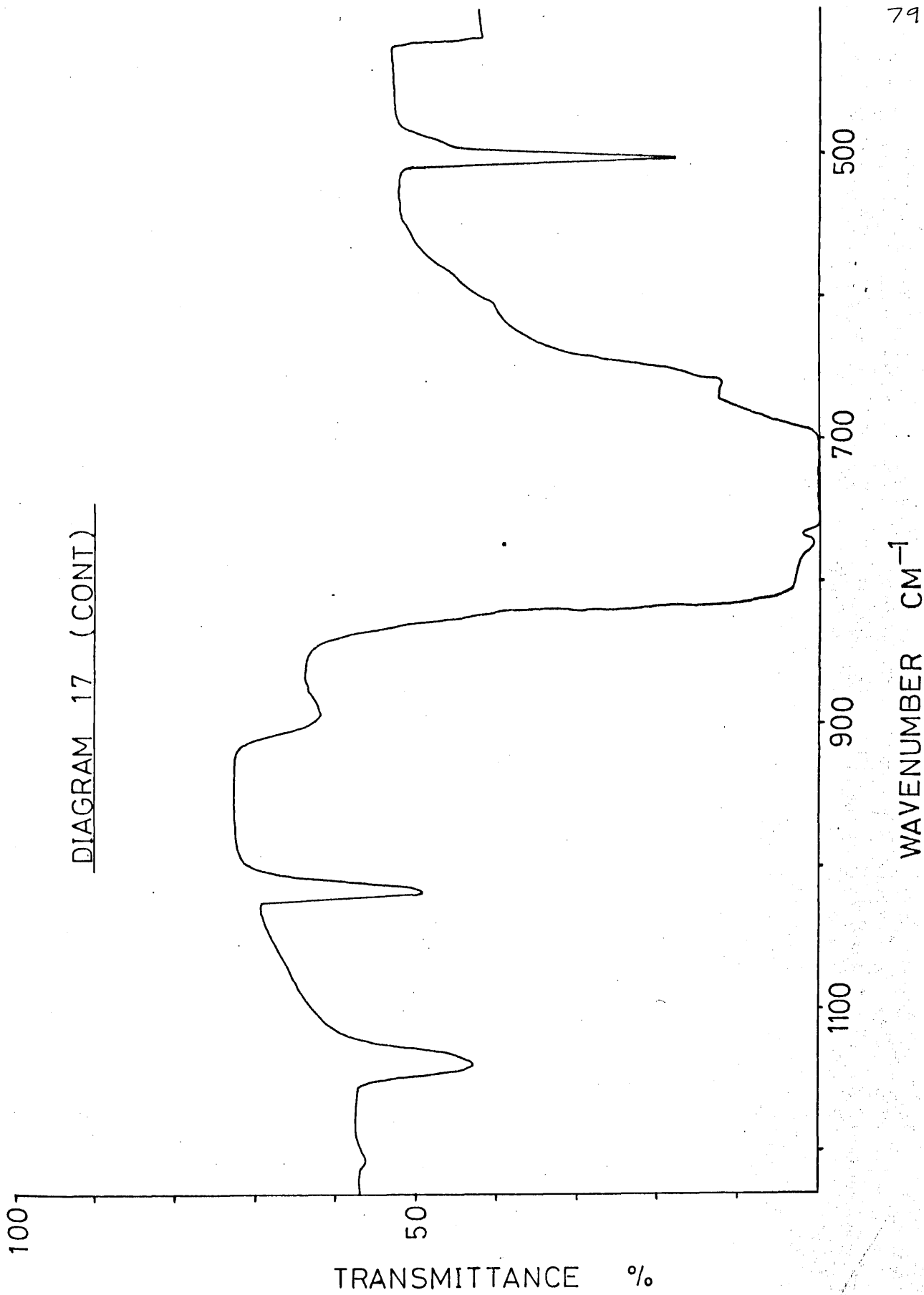
DIAGRAM 18   SOLID PHASE INFRA RED SPECTRUM OF

BORON TRIBROMIDE / CARBONYL BROMIDE

TRANSMITTANCE   %

100

50

3000

2000

WAVENUMBER   CM⁻¹

80

DIAGRAM 18 (CONT)

TRANSMITTANCE %

WAVENUMBER CM⁻¹

81
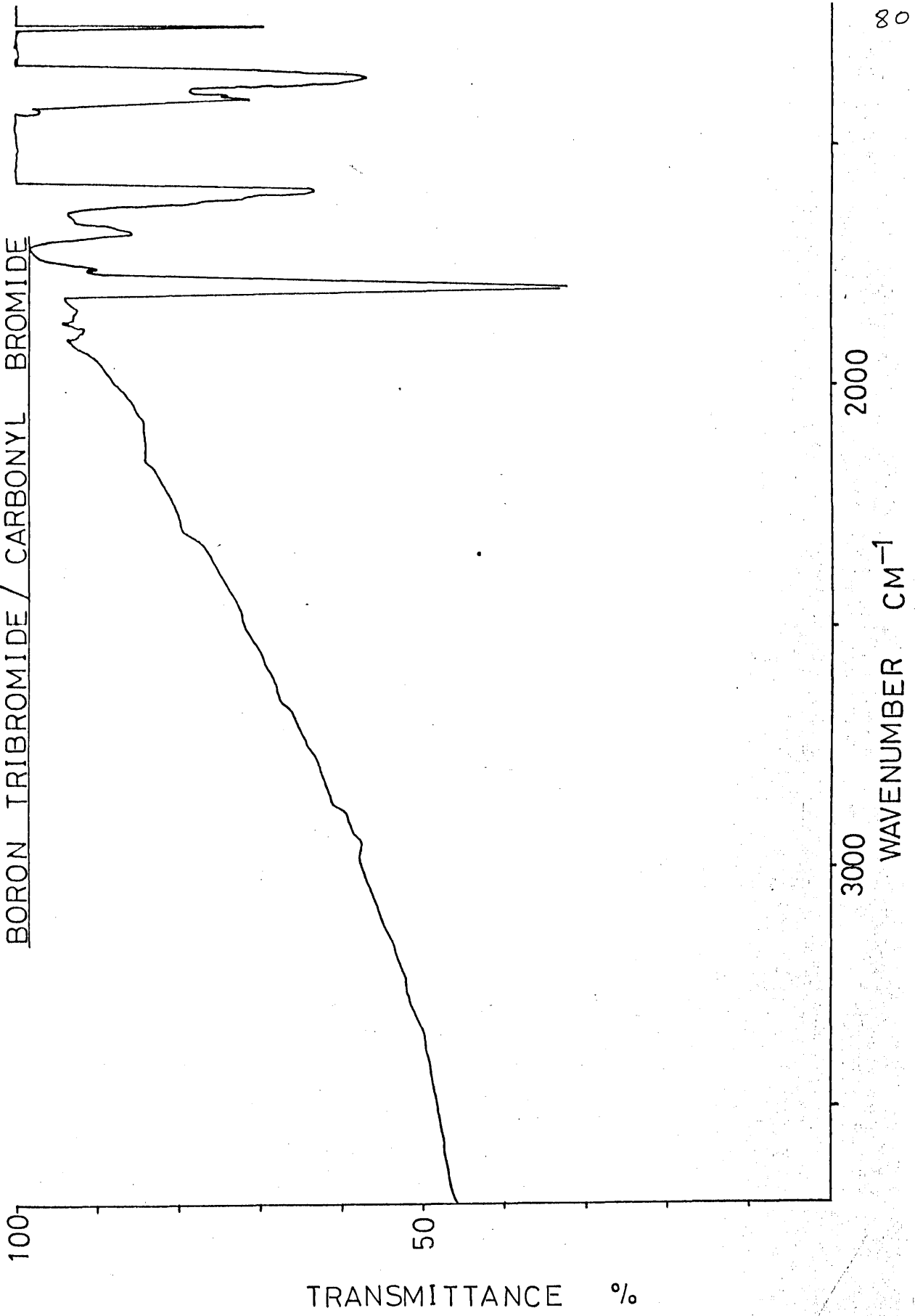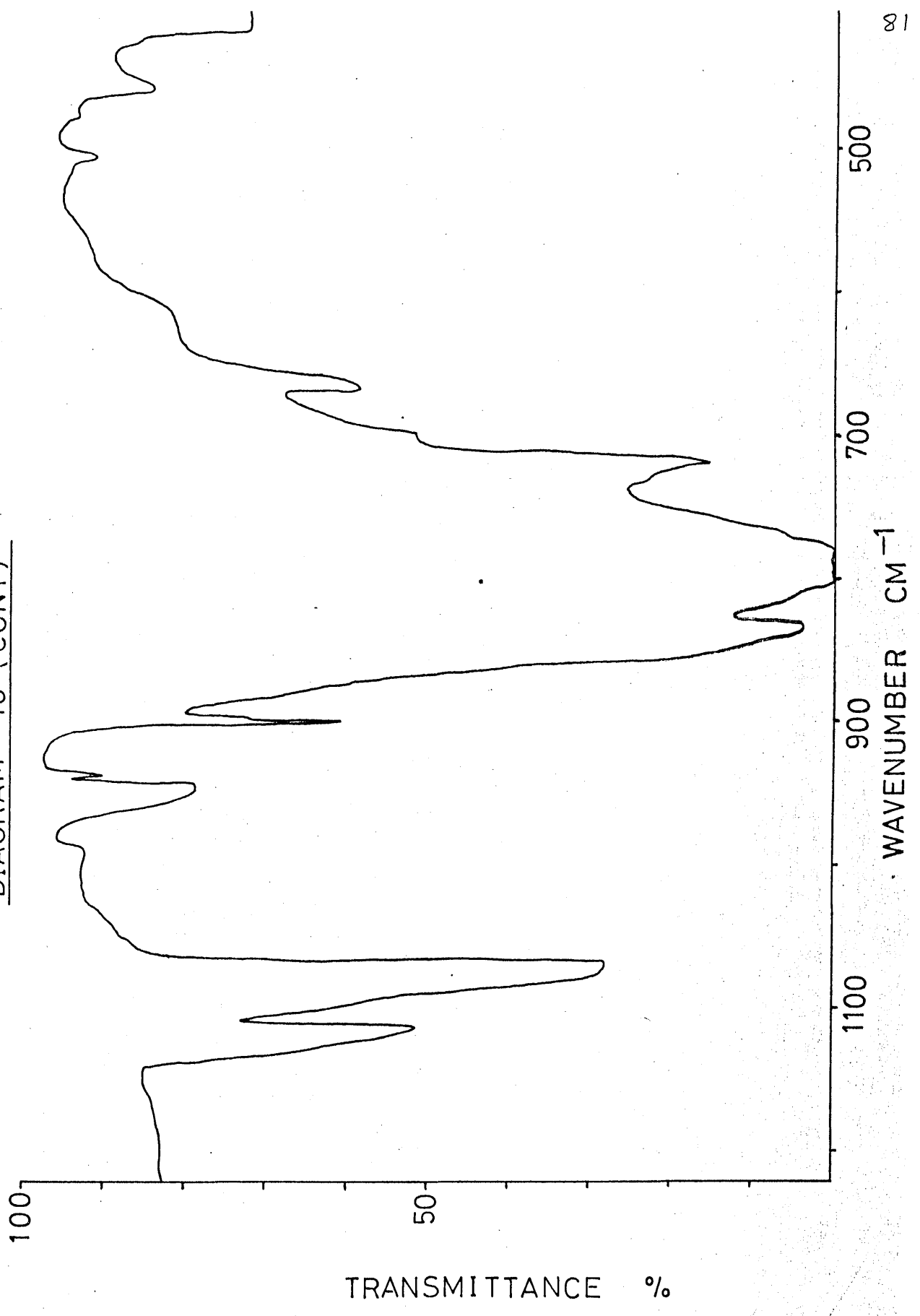
Aluminium Bromide + Carbonyl Bromide

On condensing a large excess (mole ratio ca. 5:1) of
carbonyl bromide on to aluminium bromide, a white solid mixture
resulted whilst maintained at $-196^{\circ}C$, indicating the absence
of bromine. On allowing the mixture to warm, the carbonyl
bromide melted, and the aluminium bromide floated to the
surface of the liquid. The aluminium bromide slowly dissolved,
but as it did so effervescence and the formation of a brown
colour were both clearly visible at the solid/liquid interface.
By the time room temperature had been reached, all the solid
had dissolved, and the colour had spread to give a uniformly
dark-brown solution. On pumping this solution at $-45^{\circ}C$,
where pure carbonyl bromide has a vapour pressure of ca.
10 torr[53], a dark brown solid resulted, which obviously still
contained considerable quantities of free bromine. Therefore,
the temperature was gradually raised, while still pumping,
till a white solid remained. This proved to be aluminium
bromide, recovered almost quantitatively, two experiments
giving respectively 98.5% and 97.0% of the starting weight.
This is in sharp contrast to the preparation of aluminium
chloride/carbonyl chloride complex[41], where on pumping off
excess carbonyl chloride at approximately 10 torr, the 1:1
complex remained.

Although the aluminium bromide/carbonyl bromide mixture

DIAGRAM 19   INFRA—RED SPECTRUM OF VAPOUR FROM

ALUMINIUM BROMIDE / CARBONYL BROMIDE

TRANSMITTANCE %

WAVENUMBER CM^{-1}

83
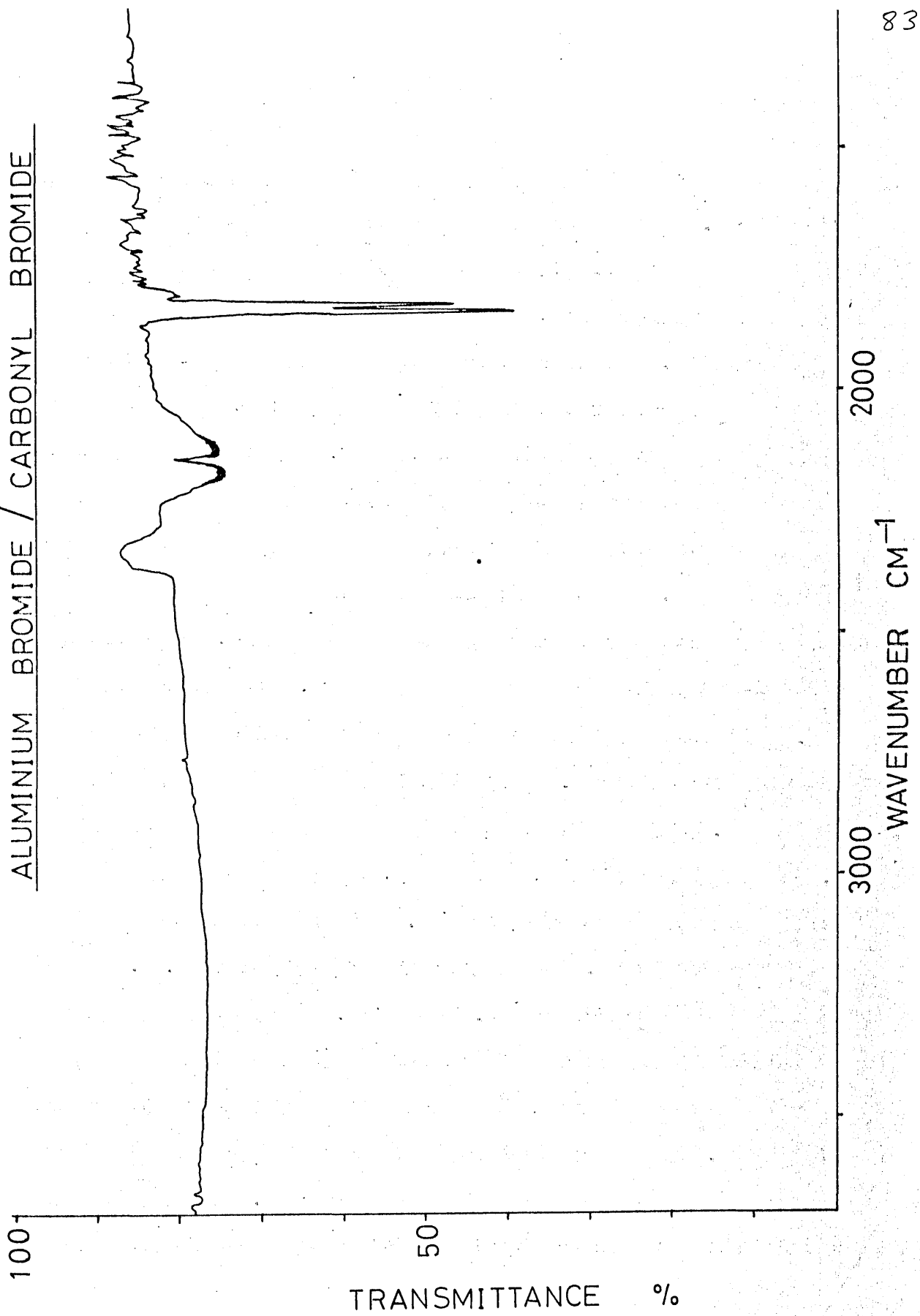
turned dark-brown within minutes while warming to room
temperature, a reference sample of pure carbonyl bromide,
kept at room temperature under otherwise similar conditions,
remained colourless. Evidently the aluminium bromide
catalysed the decomposition of carbonyl bromide, a conclusion
supported by the presence of a new, strong, band in the infra-
red spectrum of the vapour from the mixture (diagram 19).
Centred at 2150 $\pm$ 10 cm^{-1}, with well-defined P and R branches
and rotational fine structure, this band is attributable to
carbon monoxide[63].

Even when maintained at $-45^\circ C$, a freshly prepared mixture
still turned brown, though much more slowly than at room
temperature.

Aluminium Chloride + Carbonyl Bromide

Several experiments were performed, with aluminium
chloride: carbonyl bromide ratios ranging from 2:1 to 1:30.
On allowing some mixtures to slowly warm up from $-196^\circ C$, the
reaction appeared visually identical to the aluminium bromide/
carbonyl bromide system, with solid floating on the carbonyl
bromide, and gradually dissolving, accompanied by effervescence
and formation of bromine, to give a dark-brown solution.
The appearance of bromine colour was extremely rapid, reaching
its maximum intensity in well below five minutes when hand-heat
was applied to bring the system to room temperature quickly.

Even when maintained at -45°C, bromine was still formed, but only very slowly. On pumping to dryness, also at -45°C, the residue showed a weight increase far less than that predicted for a 1:1 complex. Since the residue was brown, the weight increase was probably due, at least in part, to bromine, which at -45°C is a solid with vapour pressure only ca. 1 torr[4]. This was confirmed by the appearance of brown vapour on warming the residue to room temperature. The result was:-

Starting wt. $AlCl_3$ = 0.0605 g

Final wt. residue = 0.0654 g

Hence, even at these low temperatures and pressures, there is no evidence for an isolable complex.

Two solutions, both containing a large excess of carbonyl bromide, were allowed to stand at room temperature for several hours, then pumped to dryness (when a white solid remained) and analysed. Results were:-

	(a)	(b)
Al =	0.33×10^{-3} g. atom	0.78×10^{-3} g. atom
Cl =	0.40×10^{-3} g. atom	0.71×10^{-3} g. atom
Br =	0.46×10^{-3} g. atom	1.62×10^{-3} g. atom
Wt. residue (calc) =	0.0662 g.	0.1757 g.
Wt. residue (found) =	0.0599 g.	0.1758 g.
Starting wt. $AlCl_3$ =	0.0465 g.	0.1244 g.

TABLE 11

INFRA-RED OF VAPOUR FROM ALUMINIUM CHLORIDE/CARBONYL BROMIDE

FREQUENCY cm^{-1}	ASSIGNMENT (REF. 61)	
3630 s	$2\nu_2$	COX_2
2150 s		CO
1922 w	?	
1822 vs	ν_2	COX_2
1780 m	$3\nu_5 + \nu_4$	$COBr_2$
1630 w	$2\nu_4$	$COCl_2$
1590 m	$2\nu_4$	$COClBr$
1505 m	$2\nu_4$	$COBr_2$
1480 m	$2\nu_5 + \nu_4$	$COBr_2$
1405 vw	$\nu_1 + \nu_4$	$COCl_2$
1318 m	$\nu_1 + \nu_4$	$COClBr$
1218 m	$2\nu_1 + \nu_5$	$COBr_2$
1165 m	$\nu_1 + \nu_4$	$COBr_2$
1133 w	?	
1094 w	$\nu_4 + \nu_5$	$COBr_2$
1085 w	$2\nu_6$	$COClBr$
1022 m	$2\nu_6$	$COBr_2$
960 w	?	
920 m	$\nu_3 + \nu_4$	$COBr_2$
893 s	$\nu_1 + \nu_5$	$COClBr$
851 m	ν_4	$COCl_2$
808 vs	ν_4	$COClBr$
785 vs(sh)	$\nu_1 + \nu_5$	$COBr_2$
745 vs	ν_4	$COBr_2$
610 m	$\nu_1 + \nu_3$	$COBr_2$
548 m	ν_6	$COClBr$
522 s	ν_1	$COClBr$
512 s	ν_6	$COBr_2$
426 s	ν_1	$COBr_2$

DIAGRAM 20   INFRA-RED SPECTRUM OF VAPOUR FROM

ALUMINIUM CHLORIDE / CARBONYL BROMIDE

87
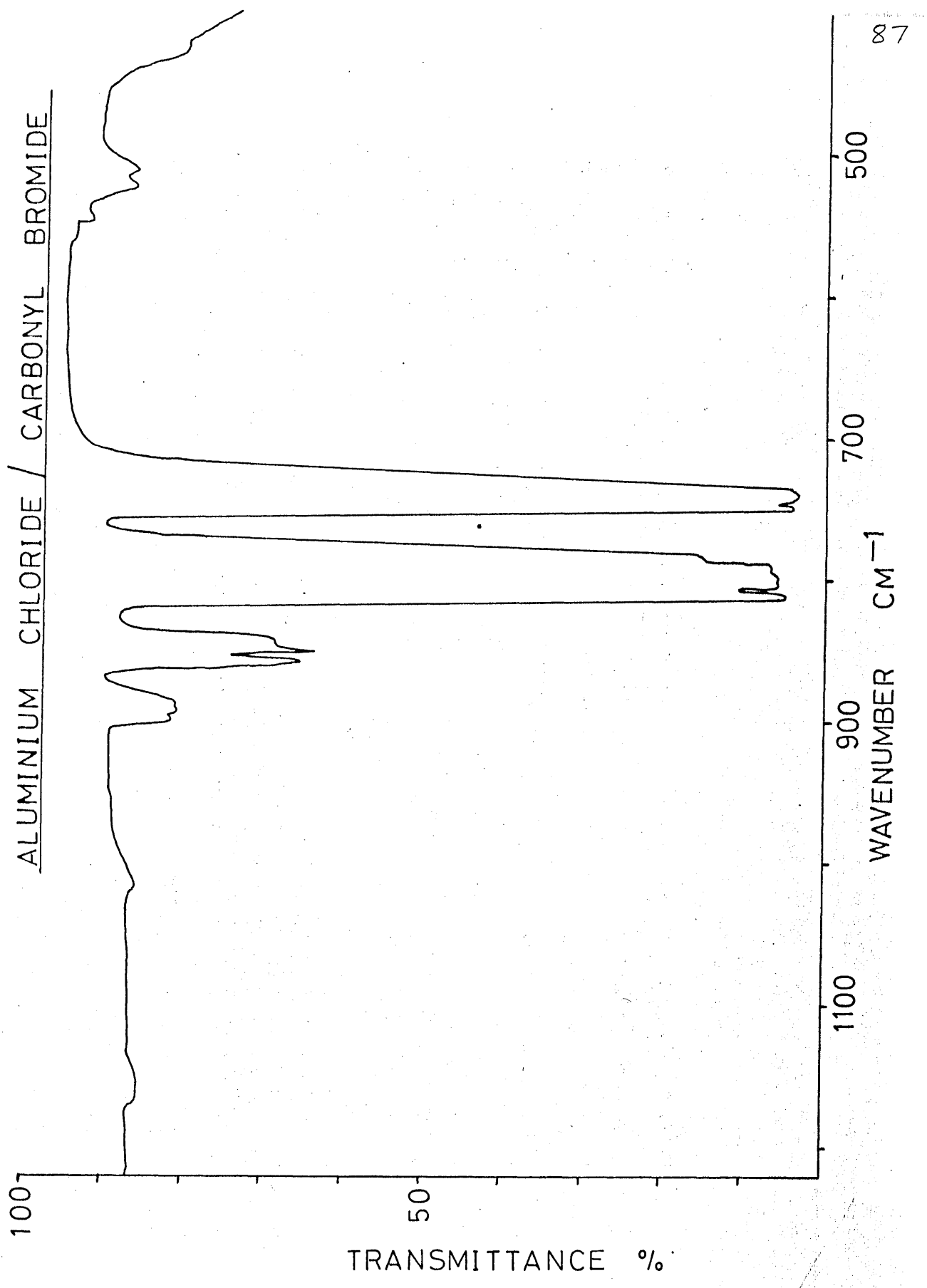
Both residues correspond to AlX_3 only, and also clearly demonstrate that halogen exchange has occurred.

Further proof of exchange came from the infra-red spectrum of the vapour from a room temperature solution, when bands for carbonyl bromide, carbonyl chlorobromide and carbonyl chloride were all clearly visible. The assignments are given in table 11, and part of a spectrum obtained at lower pressure (by expanding vapour into a larger volume) is shown in diagram 20 (compare with diagrams 14 and 21).

The much lower intensity of carbonyl chloride bands compared to the others is presumably due to

(a) The large excess of carbonyl bromide over aluminium chloride in the starting materials.

(b) Complexing of carbonyl chloride with aluminium chloride, thus reducing its vapour pressure.

Aluminium Bromide + Carbonyl Chloride

Similar results were obtained, with the solid dissolving, and formation of carbon monoxide and bromine. This occurred very rapidly at room temperature, but much more slowly at $-45^{\circ}C$.

On pumping two solutions (both with a large excess of carbonyl chloride) to dryness, one at $-45^{\circ}C$, one at room temperature, the residues showed a decrease in weight compared

to the starting aluminium bromide, ruling out any simple,
1:1 complex formation.   Results were:-

-45°C: (Brown residue)   g.

   Initial wt. $AlBr_3$ =   0.1250

   Final wt.   residue   =   0.1183

Room temperature: (White residue)

   Initial wt. $AlBr_3$ =   0.2505

   Final wt.   residue   =   0.1453

Analysis of the room temperature residue corresponded to AlX_3:

   Al = 0.97×10^{-3} g. atom

   Cl = 2.72×10^{-3} g. atom

   Br = 0.25×10^{-3} g. atom

Wt. residue (calc.) = 0.1428 g.

Wt. residue (found) = 0.1453 g.

Infra-red spectra of the vapour from a room temperature
solution again showed the presence of carbonyl chloride,
carbonyl chlorobromide, carbonyl bromide and carbon monoxide,
all in appreciable quantities (diagram 22; table 12).   The
gas phase spectrum of pure carbonyl chloride was run for
comparison purposes (diagram 21), and gives good agreement
with published spectra[64,65].

DIAGRAM 21

INFRA-RED SPECTRUM OF

CARBONYL CHLORIDE (GAS)

90

2000

3000

WAVENUMBER CM^{-1}

100

50

TRANSMITTANCE %

DIAGRAM 21 (CONT)

TRANSMITTANCE %

WAVENUMBER CM^{-1}

91
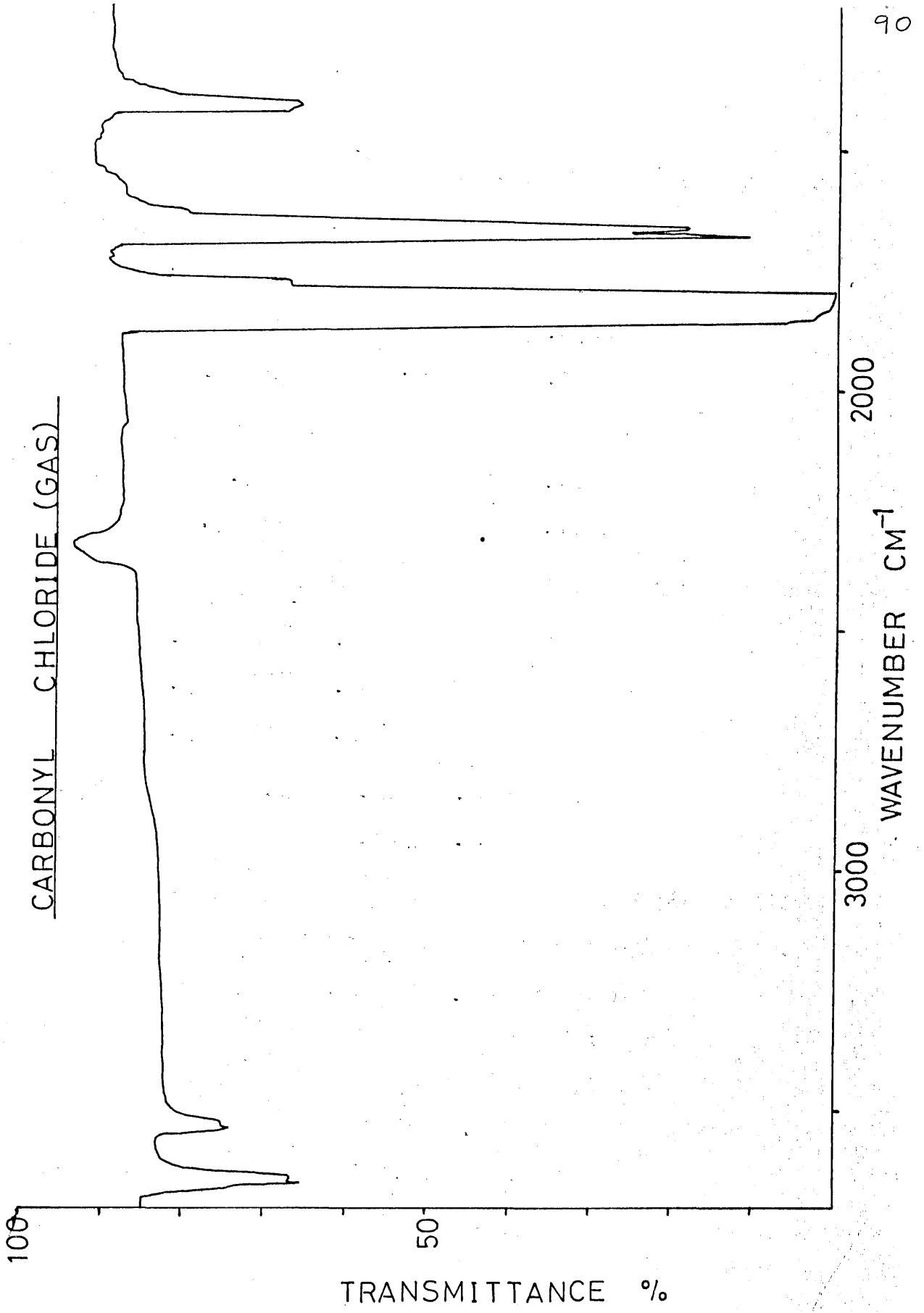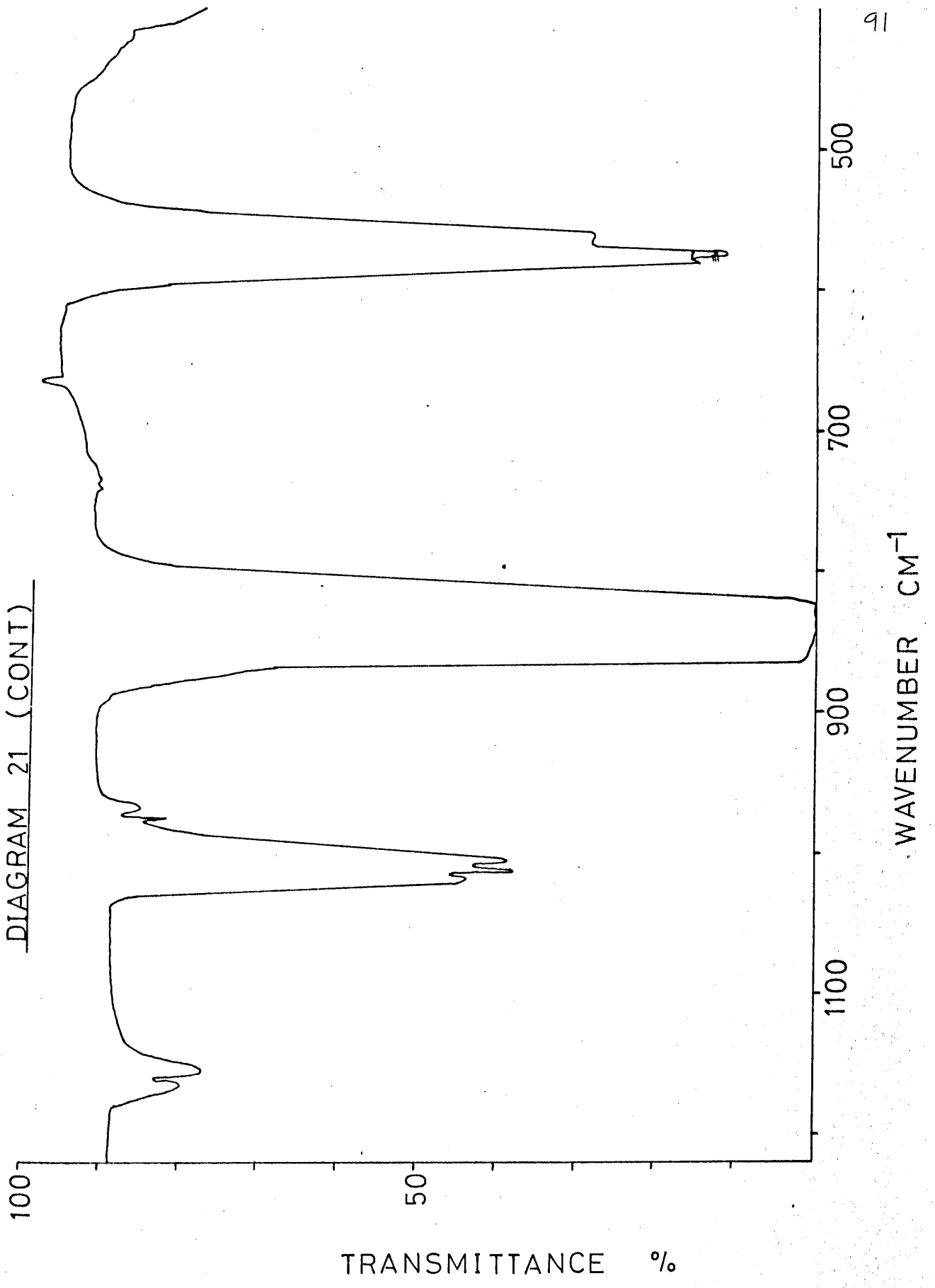
DIAGRAM 22   INFRA-RED SPECTRUM OF VAPOUR FROM
ALUMINIUM BROMIDE / CARBONYL CHLORIDE

92
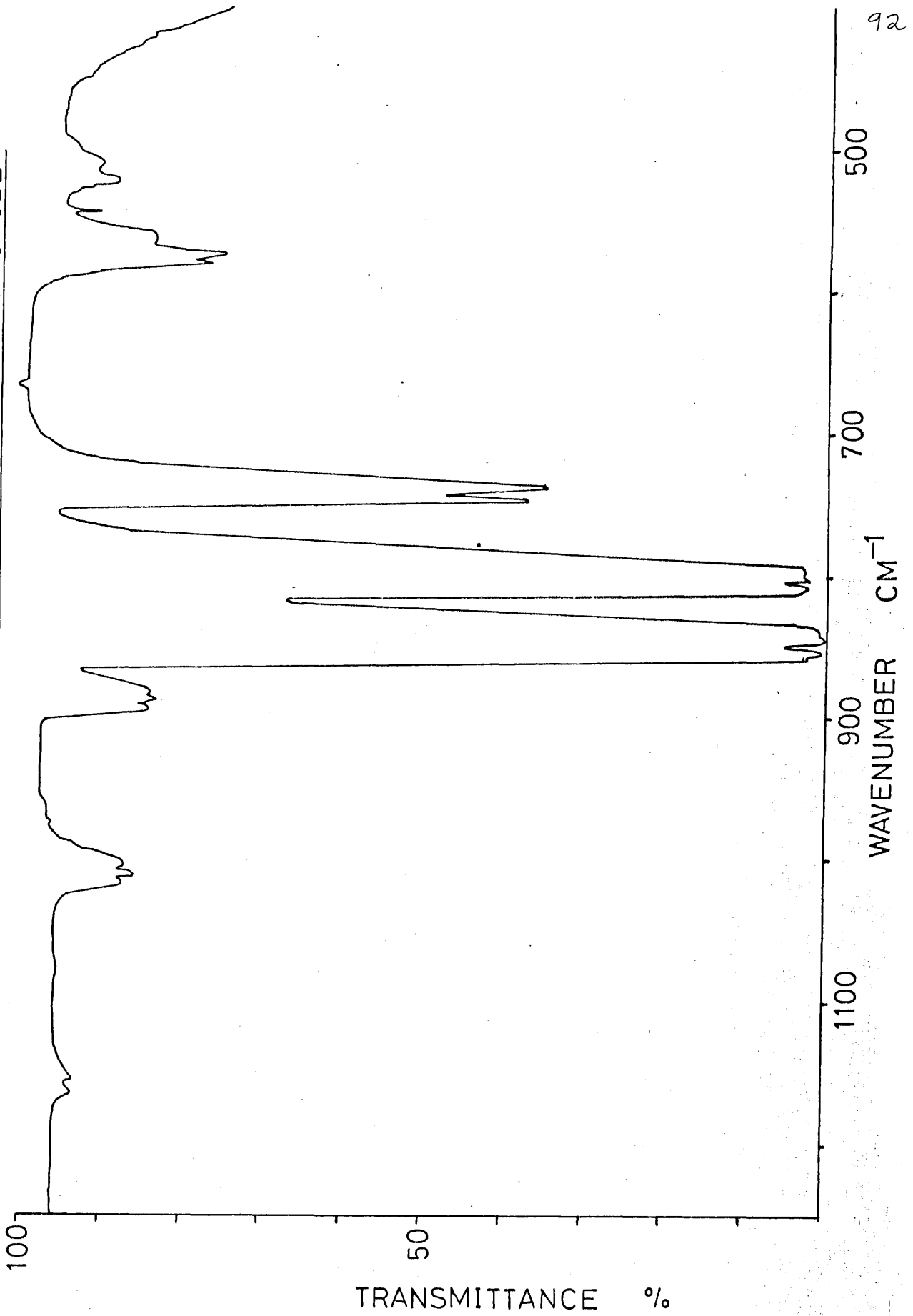
TABLE 12

INFRA-RED FREQUENCIES OF VAPOUR FROM CARBONYL CHLORIDE/

ALUMINIUM BROMIDE

FREQUENCY cm^{-1}	ASSIGNMENT (REF. 61, 64, 65)	
3630 m	$2\,\nu_2$	COX_2
2140 m		CO
1825 s	ν_2	COX_2
1680 m	$2\,\nu_4$	$COCl_2$
1595 m	$2\,\nu_4$	$COClBr$
1405 m	$\nu_1 + \nu_4$	$COCl_2$
1310 m	$\nu_1 + \nu_4$	$COClBr$
1160 m	$2\,\nu_1,\ 2\,\nu_6$	$COCl_2$
1080 w	$2\,\nu_6$	$COClBr$
1010 m	$\nu_1 + \nu_5$	$COCl_2$
970 w	?	
890 m	$\nu_1 + \nu_5$	$COClBr$
850 vs	ν_4	$COCl_2$
805 vs	ν_4	$COClBr$
780 s(sh)	$\nu_1 + \nu_5$	$COBr_2$
745 s	ν_4	$COBr_2$
580 m	ν_6	$COCl_2$
565 w(sh)	ν_1	$COCl_2$
545 w	ν_6	$COClBr$
520 m	ν_1	$COClBr$
445 vw	ν_5	$COCl_2$
425 vw	ν_1	$COBr_2$

Aluminium Iodide + Carbonyl Chloride

Mixing aluminium iodide and carbonyl chloride at $-196°C$, then allowing the mixture to warm, resulted in the white aluminium iodide slowly disappearing, presumably due to solution in the liquid carbonyl chloride though this was masked by the deposition of considerable quantities of iodine crystals. Effervescence was also observed.

Infra-red spectra of the vapour from the mixture showed only carbonyl chloride and carbon monoxide (diagram 23 shows the region $1300-400$ cm^{-1}; table 13 gives the full frequencies). By comparison with aluminium chloride/carbonyl bromide and aluminium bromide/carbonyl chloride, this would seem to suggest that both carbonyl chloroiodide and carbonyl iodide are unstable at room temperature, decomposing to carbon monoxide, iodine and carbonyl chloride. (See also Part 3).

DIAGRAM 23   INFRA—RED SPECTRUM OF VAPOUR FROM

ALUMINIUM IODIDE / CARBONYL CHLORIDE

95
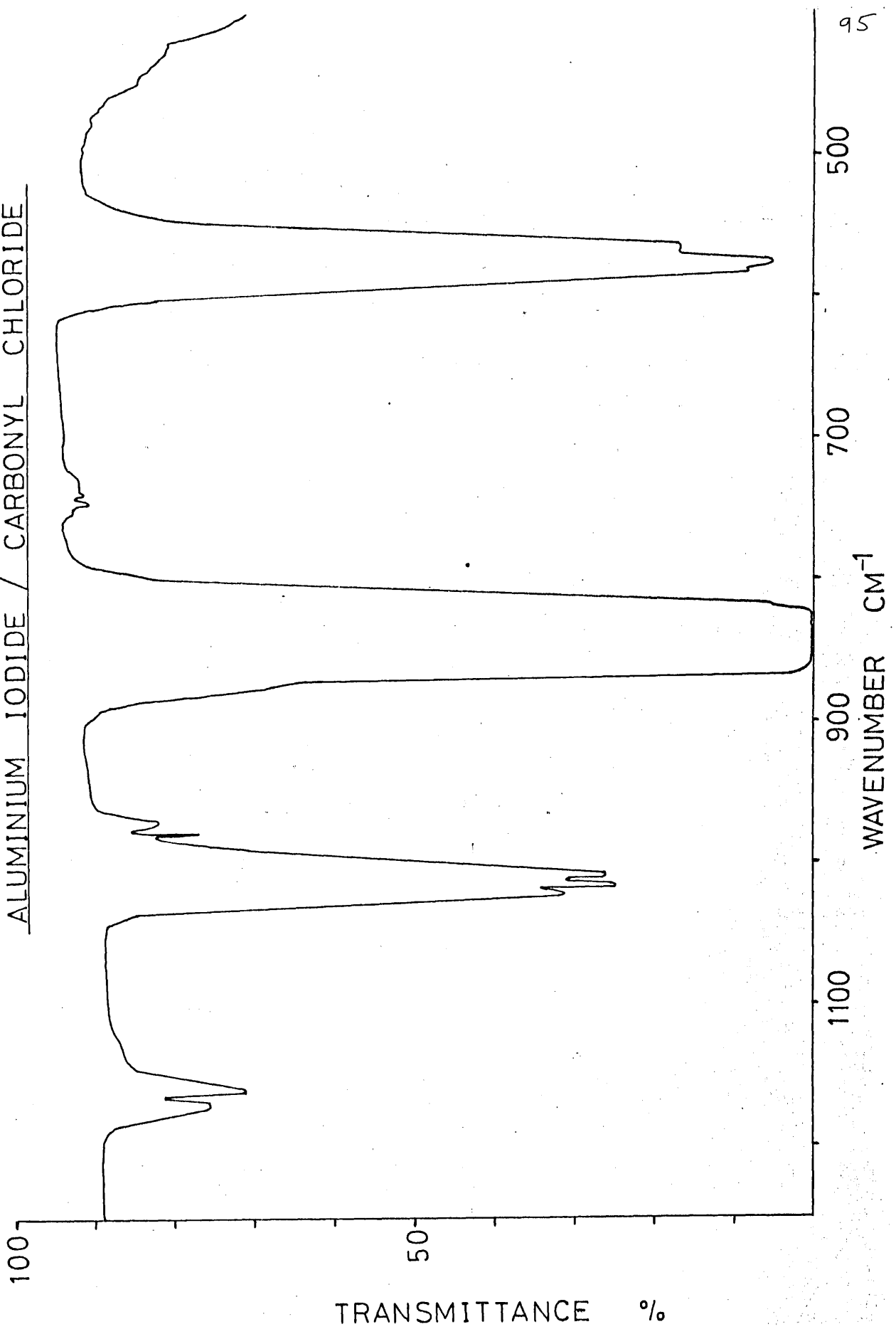
TABLE 13

INFRA-RED FREQUENCIES OF VAPOUR FROM CARBONYL CHLORIDE/

ALUMINIUM IODIDE

FREQUENCY cm^{-1}	ASSIGNMENT (REF. 64 and 65)
3630 m	$2\nu_2$ $COCl_2$
3540 m	$\nu_2 + 3\nu_1$ $COCl_2$
2150 s	CO
2070 m	$\nu_2 + \nu_5$ $COCl_2$
1828 vs	ν_2 $COCl_2$
1680 s	$2\nu_4$ $COCl_2$
1422 m	$\nu_1 + \nu_4$ $COCl_2$
1165 m	$2\nu_1, 2\nu_6$ $COCl_2$
1015 s	$\nu_1 + \nu_5$ $COCl_2$
845 vs	ν_4 $COCl_2$
745 w	$\nu_3 + \nu_5$ $COCl_2$
580 s	ν_6 $COCl_2$
567 s	ν_1 $COCl_2$

DISCUSSION

Because of the high electronegativities of the halogens, carbonyl halides might be predicted to act as poor Lewis bases compared to other carbonyls, such as organic ketones[41,66]. Such complexes as exist would be expected to be fairly unstable, a theory supported by the properties of the aluminium chloride/carbonyl chloride complex.

The present results on boron tribromide/carbonyl bromide give no evidence for complex formation, even at low temperatures, in accord with Christe's findings[42] on the boron trichloride/carbonyl chloride system. Normally, boron halides are considered better Lewis acids than aluminium halides (e.g. with phosphoryl chloride[67] and ethylacetate[43]). Yet for carbonyl halides, while aluminium chloride forms an isolable complex with phosgene, and there must be interaction in the other systems to account for halogen exchange and catalytic decomposition of carbonyl bromide, boron trichloride forms no complex, and boron tribromide does not catalyse the same decomposition. (The boron tribromide/carbonyl chloride and boron trichloride/carbonyl bromide systems remain to be studied). This discrepancy is probably due[42] to the need for boron to rehybridise from planar sp_2 to tetrahedral sp^3 on coordination, involving the loss of considerable π-bond energy

which has to be compensated by the formation of a new donor-acceptor bond. Thus if the boron-donor bond energy is less than the π-bond energy loss, no adduct would be expected. In the aluminium halides, however, the aluminium is already tetrahedrally coordinated, so the same problem does not arise.

As already stated, although no isolable complexes were found, some interaction in the systems aluminium bromide/carbonyl bromide, aluminium chloride/carbonyl bromide and aluminium bromide/carbonyl chloride must be assumed to account for the halogen exchange and the catalytic decomposition of carbonyl bromide. The speed of halogen exchange, as exemplified by

(a) the quick appearance of strong infra-red peaks for all three carbonyl halides,

(b) the rapid production of bromine,

is in contrast to the results of Huston[39,40]. For solutions of similar concentrations to those used in the present work, he found half-lives for exchange between radioactive aluminium chloride and phosgene of 30 minutes or longer at $25^{\circ}C$. In the present work, quantitative comparisons are difficult and very approximate, because of the need for cooling the systems initially to obtain the mixtures, which then slowly warm to room temperature. On applying external heat, however, to

speed the attainment of room temperature, the bromine colour
seemed to reach maximum intensity in the order of 5 minutes,
suggesting a faster exchange rate. The reason is not known,
but the fast rate suggests that exchange probably occurs
through an ionic rather than covalent mechanism. For the
concentration range involved, Huston postulated ionisation in
the system aluminium chloride/carbonyl chloride.

The presence of appreciable quantities of all three
carbonyl halides, even after standing for several hours,
suggests that the exchange is an equilibrium process, involving
several separate equilibria of the type

$$AlCl_3 + COBr_2 \rightleftharpoons [AlCl_3/AlBr_3] + COClBr \rightleftharpoons AlBr_3 + COCl_2$$

$$CO + Br_2 \qquad [AlCl_3/AlBr_3] + COCl_2 + COBr_2 + COClBr$$

$$CO + Br_2$$

In a closed apparatus, such as that used, equilibrium would be
established, but in an open system the escape of carbon monoxide
would pull the equilibria over. Even so, von Bartal's claim[45]
that only the reaction

$$AlBr_3 + 3COCl_2 \longrightarrow AlCl_3 + 3COClBr$$

takes place seems a vast oversimplification. Likewise, his
claim, based on halide analysis, that with excess aluminium

bromide, aluminium chlorobromide is formed quantitatively also seems dubious. The nature of the aluminium halides in solution, and on pumping off carbonyl halides, cannot be judged from the results available. From the variation in analytical data, however, there must be a mixture of aluminium halides, whether the simple aluminium chloride/aluminium bromide mixture or involving chemically distinguishable mixed halides. In this connection, the failure to obtain any useful Raman or infra-red spectra is unfortunate. Corbett and Gregory's assertion[46] that the residue from aluminium bromide/phosgene is an annealed mixture of aluminium chloride/ aluminium bromide is merely qualitative, with no apparent experimental backing.

The possibility remains that complexes may be formed at temperatures lower than -45°C, at which temperatures halogen exchange and carbonyl bromide decomposition might be suffic- iently slow to enable complex isolation. This is most likely with carbonyl chloride, which is liquid down to -104°C[4], whereas carbonyl bromide solidifies at a higher temperature, estimated at -70 to -80°C, (although the exact freezing point is not known) and there would be difficulty in pumping off any excess. Even if complexes were isolated at such temperatures, their study would of course present great problems due to the need to maintain them at all times at the same low temperatures to avoid decomposition.

PART THREE

THERMOCHEMICAL PROPERTIES

OF CARBONYL BROMIDE

[See also

M.E. Anthoney, P.J. Gardner and A. Finch, J. Chem. Therm.

(1970) 2 697,

a reprint of which is included at the end of this thesis].

INTRODUCTION

Three papers have been published[68,69,70] on the equilibrium

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$
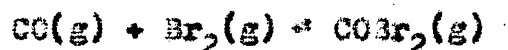
reporting equilibrium constants for temperatures ranging from 293K to 456K. Since

$$\frac{d (\ln Kp)}{d (1/T)} = \frac{\Delta H^o}{R} \quad ,$$

the enthalpy of reaction and hence the standard enthalpy of formation for carbonyl bromide could be derived. Wagman et.al.[71] used Trautz's (1915) results[68] to obtain ΔH_f^o $COBr_2(g) = -23.0$ kcal mol^{-1} [-96.2 kJ mol^{-1}], while Cox and Pilcher[72] quote a "best" value of -20.1 kcal mol^{-1} [-84.1 kJ mol^{-1}] derived from Schumacher and Bergmann's[70] work (1931). Reerink's results[69] (1928) lead to an intermediate value of -20.9 kcal mol^{-1} [-87.4 kJ mol^{-1}].

In the absence of any further experimental data, and in view of the spread of values, it was decided to redetermine ΔH_f^o employing a different, calorimetric, approach. The reaction studied was

$$COBr_2(l) + nH_2O(l) \longrightarrow CO_2(g) + [2HBr.(n-1)H_2O](l)$$

at 298.15K and one atmosphere pressure, for which the enthalpy change is denoted as ΔH hyd. By using water already saturated

with carbon dioxide for the hydrolysis, all the carbon
dioxide produced in the reaction can be considered as in its
standard (gaseous) state. Since the enthalpies of formation
of all the other reactants and products are well known,
measurement of ΔH hyd allows ΔH_f^o $COBr_2$(l) to be calculated.

Preliminary studies showed the reaction to be slow,
0.3339 g of carbonyl bromide in 200 ml of water taking ca
forty minutes to dissolve completely. Since carbonyl bromide
and water are immiscible, and shaking speeded up the reaction,
the rate of hydrolysis is probably controlled by the surface
area of the two liquids in contact. Analysis of the hydroly-
sate gave 99.5% of the calculated bromide, indicating that the
reaction goes to completion. In view of the slowness of
reaction, the use of an adiabatic solution calorimeter was
considered essential.

EXPERIMENTAL

Chemicals

The carbonyl bromide was from the same batch used previously (p. 63) [Analysis: Br (found) 84.6% by mass, Br (calc) 85.1% by mass].

Distilled water was saturated with carbon dioxide by adding a few lumps of dry ice to a flask of water which was then placed in a thermostated bath at 298K to equilibrate.

Calorimeter

The calorimeter was basically similar to that described in Part 4 (p. 131), but modified to operate adiabatically. Comprehensive details are already available[73]. The principle differences from the constant-temperature-environment calorimeter described in the next chapter were:-

(a) The calorimeter was immersed in a water jacket, the temperature of which was automatically controlled such that the temperature difference between the inside of the calorimeter and the jacket was maintained at a constant, pre-set, level (ca 0.06 $\pm$ 0.002 degrees). The design of the automatic adiabatic control was the same, with minor modifications, as that employed in the Gallenkamp Adiabatic Bomb Calorimeter[74].

(b)   As part of the adiabatic control unit, the glass Dewar
      shown in diagram 26 (p. 132) contained two additional
      thermistors.

(c)   A Scalamp galvanometer (1400 Ω) was used in place of the
      chart recorder as the out-of-balance detector in the
      thermistor bridge for measuring the temperature inside
      the calorimeter.   Readings of the thermistor resistance
      were taken every minute.

      The only modifications in the present work of the apparatus
and procedure given in reference 73 were due to the fact that
reproducible results were only obtained on eliminating all
contact between carbonyl bromide and grease.   The reason is not
known certainly, but one possible explanation is absorption of
carbonyl bromide vapour by the grease.   This was supported by
discrepancies of up to 10% in the quantity of carbonyl bromide
used as determined by weighing and comparison with the results
of post-hydrolysis bromide analysis.   To overcome this:-
(i) The ampoule design was changed slightly (diagram 24) to
enable sealing under vacuum.   The narrowed, thickened portion
facilitated sealing at a well-defined point, which meant that
the ampoule volume could be determined beforehand by weighing
first empty then filled to the constriction with water.   A
blank calorimeter run showed that the effect of heating the
ampoule during sealing, and the enthalpy of ampoule breaking,
were both negligible.
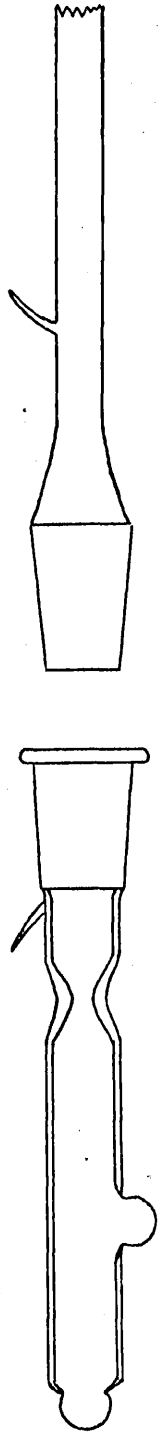
DIAGRAM 24   COBr$_2$ AMPOULE

(11) No grease was used in the calorimeter head. Tests
showed that the two flanges of the glass Dewar were waterproof
if held firmly together by a circular wire clip, and then
lightly greased on the <u>outside</u> rim only. Nor was any grease
used on the joint connecting the ampoule to the ampoule holder.

Before and after using the calorimeter for carbonyl
bromide, its performance was checked by measuring the enthalpy
of neutralization of tris(hydroxymethyl)aminomethane (THAM),
(B.D.H. Aristar grade; 99.9% minimum purity), in excess aqueous
0.1M hydrochloric acid. Results were

Before:- -7.11 kcal mol^{-1} [-29.75 kJ mol^{-1}]

After:- -7.11 kcal mol^{-1} [-29.75 kJ mol^{-1}]

Previous THAM results[73] for this calorimeter gave a mean for
ten runs of -7.11 kcal mol^{-1} [-29.75 kJ mol^{-1}] with a standard
deviation of the mean of 0.005 kcal mol^{-1} [0.02 kJ mol^{-1}].
The H_2O:THAM mole ratio varied from 1155 to 2227. These
results compare with literature values of

	DILUTION (H_2O:THAM RATIO)	ΔH^o kcal mol^{-1}	ΔH^o kJ mol^{-1}
Gunn[75]	373 - 1120	-7.107±0.001	-29.736±0.004
Sunner and Wadso[76]	1133 - 1462	-7.111±0.001	-29.752±0.004
Ojelund and Wadso[77]	1320 - 1390	-7.112±0.002	-29.757±0.008
Hill et. al.[78]	1170 - 1574	-7.109±0.001	-29.744±0.003

Procedure

After its volume had been determined, a dried ampoule
was attached, via an adaptor, to the greaseless vacuum line
described previously (p. 53), in place of the mixing vessel.
The pressure was slowly reduced to minimise the danger of
fracturing the fragile glass bulbs, and the ampoule tested for
its ability to hold a pressure $\ll 10^{-4}$ torr. Carbonyl bromide
was then condensed in by cooling the lower bulb in a solid
carbon dioxide/acetone bath ($-80^\circ C$). [The bulbs were found
to crack at liquid nitrogen temperatures]. With the $-80^\circ C$
bath still in position, the ampoule was sealed at the con-
striction, using as small a torch flame as possible. At $-80^\circ C$,
the low vapour pressure of acetone combined with the carbon
dioxide gas evolved was sufficient to avoid ignition of the
acetone. The carbonyl bromide was allowed to warm to room
temperature, and the completion of the seal tested by the
ability of the system above the constriction to hold pressures
$\ll 10^{-4}$ torr.

The ampoule was removed from the vacuum line, attached to
the holder by platinum wire, and placed in position, together
with the other inserts, in the glass Dewar. After pipetting
in 200 ml of carbon dioxide-saturated water, the Dewar was
lowered into the adiabatic jacket and allowed to equilibrate.

The quantity of carbonyl bromide used was determined by
analysis after the reaction and calibration.   10 ml samples
from the 200 ml total were titrated for bromide against 0.1N
silver nitrate solution, using eosin indicator.

RESULTS

On breaking ampoules of carbonyl bromide into water, the heavier carbonyl bromide sank to the bottom, where it was broken into small globules by the stirring. Effervescence was observed at the carbonyl bromide - water interfaces due to the production of carbon dioxide gas.

The graph for a typical reaction (No. 3 in table 14) is shown in diagram 25. The calibration graph is similar except that the heating period corresponding to the reaction period is linear rather than curved because the electric heater supplies heat at a uniform rate, whereas in the reaction the rate of heating decreases as the amount of carbonyl bromide decreases.

Assuming the heat capacity of the solution remains unchanged throughout (a valid assumption for very dilute solutions such as those used)

$$\frac{\Delta H\ reaction}{\Delta T\ reaction} = \frac{\Delta H\ calibration}{\Delta T\ calibration}$$

ΔH calibration = (Power through heater) x (heating time)

whence

$$\Delta H\ reaction\ (kcal\ mol^{-1}) = \frac{P\ x\ t}{4154} \times \frac{1}{m} \times \frac{\Delta T\ reaction}{\Delta T\ calibration}$$

REACTION TRACE FOR

$COBr_2$ CALORIMETRY

DIAGRAM 25

Time of ampoule breaking

R_1

R_2

THERMISTOR RESISTANCE (Ω)

4620

10

4600

90

80

70

4560

TIME (MINUTES)

10   20   30   40   50

HI
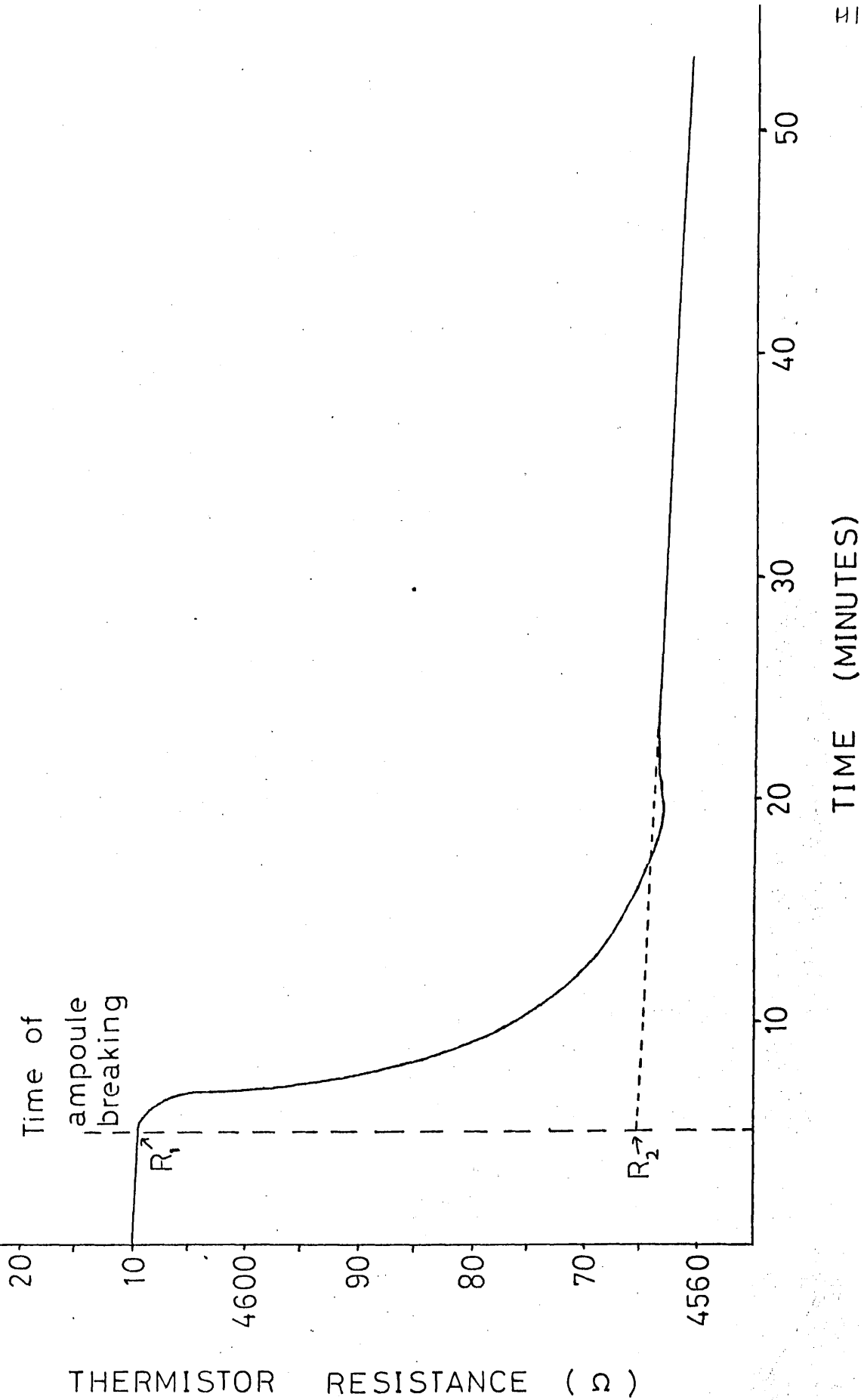
where P = Power through heater (IxV joules)

t = Heating time

m = No. moles $COBr_2$ used

ΔT = Temperature rise

4184 = Conversion factor, joules to kcal.

It can be readily shown (reference 73, p.221) that, to an accuracy of 99.9%, for a thermistor

$$\frac{\Delta T \text{ reaction}}{\Delta T \text{ calibration}} = \frac{\Delta \log R \text{ reaction}}{\Delta \log R \text{ calibration}} = \frac{\log \frac{R_1}{R_2}}{\log \frac{R_3}{R_4}}$$

where R_1 = Resistance corresponding to temperature before reaction

R_2 =   "   "   "   "   after reaction.

R_3 =   "   "   "   "   before calibration.

R_4 =   "   "   "   "   after calibration.

Since under adiabatic conditions the rate of heat loss can be assumed constant (compare the similar slopes for fore- and after-periods in diagram 25), the resistances R_2 and R_4 corresponding to the temperatures after reaction and after calibration can be determined simply by extrapolating the relevant after-periods back to the times of ampoule breaking and switching on the heater respectively.

Table 14 gives the results for nine determinations of
ΔH hyd:

$$nH_2O(l) + COBr_2(l) \xrightarrow{\Delta H \text{ hyd}} CO_2(g) + [2HBr.(n-1)H_2O](l)$$
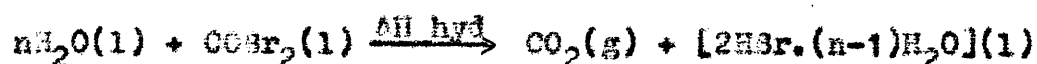
TABLE 14

ENTHALPY OF HYDROLYSIS OF CARBONYL BROMIDE

RUN NUMBER	NO.MOLES $COBr_2$ USED $(\times 10^3)$	$-\Delta H$ obs (kcal mol^{-1})	ΔH corr (kcal mol^{-1})	n (MOLE RATIO H_2O : $COBr_2$)	$-\Delta H$ hyd (kcal mol^{-1})
1	1.982	49.01	0.05	5587	48.96
2	1.028	49.06	0.12	10777	48.94
3	1.194	49.49	0.11	9277	49.38
4	1.154	48.37	0.09	9594	48.28
5	1.197	48.56	0.11	9253	48.45
6	1.359	49.16	0.10	8141	49.06
7	1.779	49.68	0.06	6224	49.62
8	2.056	49.61	0.06	4384	49.56
9	0.450	49.61	0.30	24615	49.31

The column headed ΔH corr gives the corrections applied
to the observed enthalpies of reaction to allow for some
carbonyl bromide being present as vapour. The latent heat
of vaporization, ΔH vap, and the vapour pressure, P, of
carbonyl bromide are both known at 298K[53] [7.4 kcal mol^{-1} and
190 torr respectively], and by measuring the volume, V, of the

ampoule (neglecting the small volume of $COBr_2(1)$), the correction becomes

$$\Delta H \; corr = \frac{\Delta H \; vap \times P \times V}{m \times R \times 298.15} = 7.56 \times 10^{-5} \; \frac{V}{m} \; kcal \; mol^{-1}$$

where V = Volume in ml of ampoule

m = No. moles $COBr_2$ used

R = Gas constant, 1.99×10^{-3} kcal $K^{-1}mol^{-1}$

or 62.360×10^{3} ml torr $K^{-1}mol^{-1}$

In calculating ΔH hyd, thermal effects arising from the decreased solubility of carbon dioxide with the small temperature rise during reaction, and also from the mixing of $CO_2(aq)$ and $HBr(aq)$ were ignored. Nor was account taken of the increase in pressure due to the carbon dioxide produced.

From table 14, a mean value of

$$\Delta H \; hyd = -49.06 \pm 0.16 \; kcal \; mol^{-1} \; [-205.36 \pm 0.67 \; kJ \; mol^{-1}]$$

is obtained. The uncertainty interval is calculated as $\pm$ one standard deviation of the mean, $\left[\dfrac{\Sigma d^2}{n(n-1)} \right]^{\frac{1}{2}}$

following the recommendations of Rossini[79].

DISCUSSION

Standard Enthalpy of Formation of Carbonyl Bromide

From the equation for the hydrolysis of carbonyl bromide,
it is apparent that the standard enthalpy of formation, ΔH_f^0,
of carbonyl bromide is given by

$$\Delta H_f^0 \ COBr_2(l) = \Delta H_f^0 \ CO_2(g) + 2\Delta H_f^0 \ [HBr \ in \ \tfrac{1}{2} \ (n-1)H_2O]$$
$$-\Delta H_f^0 \ H_2O - \Delta H \ hyd.$$

Using accepted values[71],

$\Delta H_f^0 \ CO_2(g)$ $= -94.05 \pm 0.01 \ kcal \ mol^{-1} \ [-393.51 \pm 0.04 \ kJ \ mol^{-1}]$

$\Delta H_f^0 \ H_2O(l)$ $= -68.315 \pm 0.001 \ kcal \ mol^{-1} \ [-285.830 \pm 0.004 \ kJ \ mol^{-1}]$

$\Delta H_f^0 [HBr \ in \ \tfrac{1}{2}(n-1)H_2O] = -29.01 \pm 0.01 \ kcal \ mol^{-1} \ [-121.38 \pm 0.04 \ kJ \ mol^{-1}]$

(mean value between n = 5000 and n = 25000)

this gives

$\Delta H_f^0 \ COBr_2(l) = -34.70 \pm 0.21 \ kcal \ mol^{-1} \ [-145.18 \pm 0.88 \ kJ \ mol^{-1}]$.

Using Schumacher and Lenher's[53] value of $7.4 \ kcal \ mol^{-1}$
(no errors assignable) for the latent heat of vaporization,
this gives

$\Delta H_f^0 \ COBr_2(g) = -27.3 \ kcal \ mol^{-1} \ [-114.2 \ kJ \ mol^{-1}]$

differing markedly from the values derived by equilibrium
studies[68,69,70]. The reason for this is not known definitely,
but in view of the differences between equilibrium constants

for similar temperatures quoted in the three papers, one possibility is that true equilibrium was not achieved in some or all of the experiments. This would be in accord with the fact that the decomposition of carbonyl bromide (and hence presumably the attainment of equilibrium) is known to be very slow.

Thermodynamic Functions for Carbonyl Halides

Overend and Evans[61] calculated the statistical thermodynamic functions for carbonyl bromide from infra-red frequency measurements, using the harmonic oscillator/rigid rotor approximations[80]. This gave

$$S^\circ \; COBr_2(g), \; 298.15K = 73.82 \; cal \; K^{-1} mol^{-1}$$

Using the following values[81]

$$S^\circ \; C \; (graphite) = 1.3609 \; cal \; K^{-1} mol^{-1}$$

$$\tfrac{1}{2} S^\circ \; O_2(g) = 24.502 \; cal \; K^{-1} mol^{-1}$$

$$S^\circ \; Br_2(l) = 36.4 \; cal \; K^{-1} mol^{-1}$$

$$S^\circ \; Br_2(g) = 58.639 \; cal \; K^{-1} mol^{-1}$$

the standard entropy of formation of carbonyl bromide is derived

$$\Delta S_f^\circ \; COBr_2(g) = 11.6 \; cal \; K^{-1} mol^{-1} \; [standard \; state \; Br_2(l)]$$

$$-10.7 \; cal \; K^{-1} mol^{-1} \; [standard \; state \; Br_2(g)]$$

From ΔS_f° and ΔH_f°,

$$\Delta G_f^\circ \; COBr_2(g) = -30.7 kcal \; mol^{-1}$$

These values are compared with those[71] for carbonyl fluoride
and carbonyl chloride in table 15.

<div align="center">TABLE 15</div>

<div align="center">THERMODYNAMIC FUNCTIONS FOR $COX_2(g)$</div>

	COF_2	$COCl_2$	$COBr_2$
$-\Delta H_f^o$ kcal mol^{-1}	151.7	52.3	27.3
$-\Delta G_f^o$ kcal mol^{-1}	143.0	48.9	30.7
$-\Delta S_f^o$ cal K^{-1}mol^{-1}	12.4	11.4	-11.6 (10.7)

The reason for deriving the entropy of formation of
carbonyl bromide from both liquid and gaseous bromine can be
seen from table 15. An apparently anomalous value for the
standard entropy of formation is due to the condensed standard
state of bromine; as shown, a steady progression is obtained
using the value for bromine gas.

Carbonyl Iodide

It is interesting at this stage to consider how table 15
might be extended to include carbonyl iodide, COI_2. There are
no reports in the literature of its preparation, and the
results in Part Two (p. 94) suggest it is very unstable even at
-45°C. Molecular models using 'planar' carbon are easily made,
and there is no reason to assume adverse structural features;
hence consideration of its thermodynamic stability is appropriate.

The first need is for an estimate of ΔH_f^0 for carbonyl
iodide. Although many bond-energy schemes have been devised
to assess $\Delta H_f^0(g)$[72], none of them is appropriate in the present
example because no "correction parameters" are available to
allow for two halogen atoms being bonded to the same carbonyl
group, a situation unique to the carbonyl halides. As an
example, the values for $\Delta H_f^0(g)$ calculated (without correction
factors) from the schemes of Laidler[72,82], Allen[72,83] and Cox[84]
are compared with the experimental values in table 16.

TABLE 16

$-\Delta H_f^0$ $COX_2(g)$, ESTIMATED FROM BOND-ENERGY SCHEMES

	$(kcal\ mol^{-1})$		
	COF_2	$COCl_2$	$COBr_2$
Experimental	151.7	52.3	27.3
Laidler[72,82]	119.3	38.2	16.0
Allen[72,83]	102.7	31.3	8.4
Cox[84]	115.5	37.5	11.5

In view of the small differences in C=O bond lengths[85]
in going from COF_2 to $COBr_2$, as shown in table 17, (compare
with COH_2 or $CO(CH_3)_2$ for example), a reasonable starting
point would seem to be the assumption of a constant bond energy
for the carbonyl group.

TABLE 17

BOND LENGTHS IN $COX_2(g)$ [n.m.]

	C=O	C-X
COF_2	0.117 ± 0.002	0.132 ± 0.002
$COCl_2$	0.1166 ± 0.0002	0.1746 ± 0.0004
$COBr_2$	0.113 ± 0.002	0.205 ± 0.004
COH_2	0.121	-
$CO(CH_3)_2$	0.124	-

From the cycle

$$C(g) + O(g) + 2X(g) \xleftarrow{\Sigma \text{ DISSOCIATION ENERGIES}} COX_2(g)$$

ΔH atomization $\qquad\qquad\qquad\qquad\qquad\qquad\qquad \Delta H_f^o$

$$C(graphite) + \tfrac{1}{2}O_2(g) + X_2(\text{standard state})$$
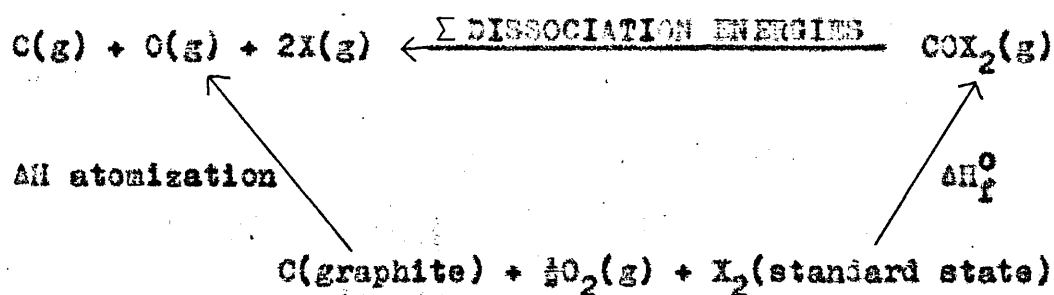
$\Delta H_f^o \; COX_2(g) = \Delta H$ atomization $- 2\bar{D}(C-X) - D(C=O)$

where

$\bar{D}(C-X)$ is the mean bond dissociation energy for the C-X bond, and $\bar{D}(C=O)$ is defined by the relation

$\bar{D}(C=O) =$ Dissociation Energies $- 2\bar{D}(C-X)$

Using values from reference 71,

ΔH atomization

$\qquad$ X = F $\quad$ 268.60 kcal mol^{-1}

$\qquad\qquad$ Cl $\quad$ 289.01 kcal mol^{-1}

$\qquad\qquad$ Br $\quad$ 284.32 kcal mol^{-1}

The values of $\bar{D}(C-X)$ used were those for $CX_4(g)$[71], since, despite the change in hybridisation of the carbon atom (which would be expected to have only a small effect[84]), of all the simple organic halides the bond lengths[85] in CX_4 came closest to those in COX_2 (table 18)

<u>TABLE 18</u>

CX_4 BOND LENGTHS AND MEAN BOND DISSOCIATION ENERGY

	Bond length (nm)	$\bar{D}(C-X)$ kcal mol^{-1}
$CF_4(g)$	0.1323 ± 0.0005	117.0
$CCl_4(g)$	0.1766 ± 0.0003	73.1
$CBr_4(g)$	0.1942 ± 0.0003	64.7

Using the values for $\bar{D}(C-X)$ in table 18,

$$\bar{D}(C=O) \; COF_2 = 186 \text{ kcal mol}^{-1}$$
$$COCl_2 = 185 \text{ kcal mol}^{-1}$$
$$COBr_2 = 182 \text{ kcal mol}^{-1}$$

in accord with the initial assumption.

Despite the approximate and empirical nature of the method, the good agreement obtained justifies extending it to carbonyl iodide, where

$$\Delta H \text{ atomization} = 231.9 \text{ kcal mol}^{-1}$$

$$\bar{D}(C=O) = 185 \text{ kcal mol}^{-1} \text{ from above.}$$

Unfortunately, data for CI_4 are not available, so $\bar{D}(C-X)$ has to be extrapolated from values for CH_3I and CH_2I_2 by comparison with the other halides (table 19).

TABLE 19

MEAN C-X BOND DISSOCIATION ENERGY FOR CH_nX_{4-n}

	ΔH_f^0 kcal mol^{-1}	TOTAL DISSOCIATION ENERGY kcal mol^{-1}	$\bar{D}(C-X)$ kcal mol^{-1}
CBr_4	19	259.3	64.7
$CHBr_3$	4	299.6	67.7
CH_2Br_2	-	-	-
CH_3Br	-8.4	362.7	68.1
CCl_4	-24.6	312.2	78.1
$CHCl_3$	-24.7	335.3	79.6
CH_2Cl_2	-22.1	355.7	80.6
CH_3Cl	-19.3	376.0	81.4
CI_4	-	-	-
CHI_3	-	-	-
CH_2I_2	27.0	299.6	52.6
CH_3I	3.1	350.0	55.4

[Relevant values for D(C-H) taken from Laidler[72] and Cox[84]]

This gives $\bar{D}(C-I)$ $\underline{ca}$ 50 kcal mol^{-1}

from which

ΔH_f^0 $CCl_2(g)$ = -3 $\pm$ $\underline{ca}$ 5 kcal mol^{-1}

$[-13 \pm 20\ kJ\ mol^{-1}]$

Using Kubaschewski and Evans'[86] procedure for the estimation of entropies

$$S^0_{298} \; COI_2(g) = 39.0 + 0.34M - 6.2 \times 10^{-4}M^2$$
$$(cal \; K^{-1}mol^{-1})$$

where M = Molecular weight COI_2, 281.81

leads to

$$S^0_{298} \; COI_2(g) = 86 \; cal \; K^{-1}mol^{-1}$$

whence

$$\Delta S^0_f \; COI_2(g) = 32 \; cal \; K^{-1}mol^{-1}$$

[-2 cal K^{-1} mol^{-1} if standard state of iodine is taken as gas]

and

$$\Delta G^0_f \; COI_2(g) = -13 \pm \underline{ca} \; 10 \; kcal \; mol^{-1}$$

Clearly, however, carbonyl iodide would be expected to exist as a condensed phase in its standard state. By comparison with the other carbonyl halides, the latent heat of vaporization is likely to be $\underline{ca}$ 8 kcal mol^{-1} [COF_2 $\underline{ca}$ 4 kcal mol^{-1} $COCl_2$ 6 kcal mol^{-1}, $COBr_2$ 7.4 kcal mol^{-1}][81]. The entropy of vaporization for molecular compounds is usually close to the Trouton figure of 22 cal K^{-1} mol^{-1}, giving

$$\Delta H^0_f \; COI_2 \; (l) \quad \underline{ca} \quad -11 \; kcal \; mol^{-1}$$
$$\Delta S^0_f \; COI_2 \; (l) \quad \underline{ca} \quad 10 \; cal \; K^{-1}mol^{-1}$$
$$\Delta G^0_f \; COI_2 \; (l) \quad \underline{ca} \quad -14 \; kcal \; mol^{-1}$$

Dissociation Equilibria

In view of the great variation in stabilities for the carbonyl halides, it is interesting to compare the equilibrium constants at 298.15K for the dissociation

$$COX_2(g \text{ or } l) \rightleftharpoons CO(g) + X_2 \text{ (s-s)}$$
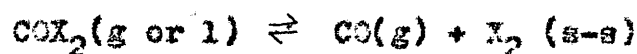
The necessary data are given in table 20.

TABLE 20

ENTHALPY, ENTROPY AND FREE ENERGY OF DISSOCIATION

FOR CARBONYL HALIDES

	ΔH diss. kcal mol^{-1}	ΔS diss. cal K^{-1}mol^{-1}	ΔG diss. kcal mol^{-1}
$COF_2(g)$	125.3	33.7	115.2
$COCl_2(g)$	25.9	32.7	16.1
$COBr_2(g)$	0.9	9.8	-2.1
(1)	8.3	31.8	-1.2
$COI_2(g)$	-23	-11	-20
(1)	-8	11	-19

From these values, the equilibrium constants, Kp, for dissociation are derived as

$COF_2(g)$	4.7×10^{-85}
$COCl_2(g)$	1.6×10^{-12}
$COBr_2(g)$	34.4
(1)	7.6
$COI_2(g)$	4×10^{14}
(1)	8×10^{13}

PART FOUR

THERMOCHEMICAL PROPERTIES

OF

ALUMINIUM HALIDES

INTRODUCTION

Though the literature contains several determinations of the standard enthalpy of formation of aluminium chloride, the values for aluminium bromide and aluminium iodide have been much less thoroughly investigated, and rely mostly on fairly old work. Table 21 lists the literature data.
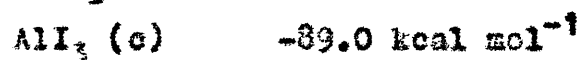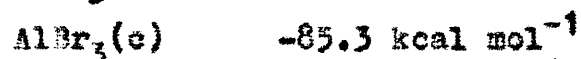
TABLE 21

LITERATURE VALUES FOR THE ENTHALPIES OF FORMATION OF

ALUMINIUM HALIDES

AUTHORS	REFER- ENCES	YEAR		$-\Delta H_f(c)$ kcal mol^{-1}			TEMP. K
				AlCl$_3$ *	AlBr$_3$ *	AlI$_3$ *	
Berthelot	87, 71	1878	a	170.6	126.8	77.6	282
			b	–	124.6	75.9	282
Klemm and Tanke	88, 90	1931)	c	167	121	71	293
Klemm and Jacobi	89	1932)					
Siemonsen	91	1951	d	167.5	–	–	298
Dear and Eley	96, 81, 95	1954	e	–	–	75.2	298
Corbett and Gregory	92, 95	1954	f	–	–	73.7	298
Coughlin	93	1958	g	168.57	–	–	298
Gross and Hayman	94	1967	h	168.80	–	–	298

* The nature of the crystal structures is irrelevant to the present work. "AlX$_3$" is used only as an abbreviation for "aluminium halide", and is not intended to suggest that the crystals consist of AlX$_3$ units.

(a) Calculated using Berthelot's values for the enthalpies
of solution in water at 282 K,

$$AlCl_3(c) \qquad -76.3 \text{ kcal mol}^{-1}$$

$$AlBr_3(c) \qquad -85.3 \text{ kcal mol}^{-1}$$

$$AlI_3(c) \qquad -89.0 \text{ kcal mol}^{-1}$$
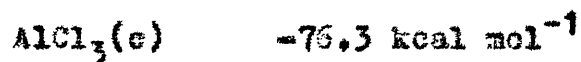
and ΔH_f^O $Al^{3+}(aq)$ and ΔH_f^O $X^-(aq)$ from reference 71, assuming
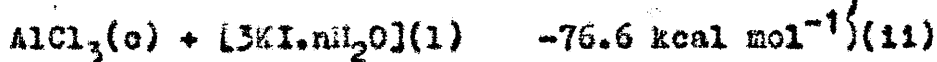
$$AlX_3(c) \xrightarrow{H_2O} Al^{3+}(aq) + 3X^-(aq)$$
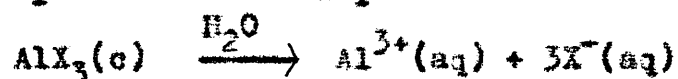
[after the JANAF tables[95]].

(b) Berthelot also measured the enthalpies of solution:

$$AlBr_3(c) + [3KCl.nH_2O](l) \qquad -86.9 \text{ kcal mol}^{-1} \Big) \text{ (i)}$$

$$AlCl_3(c) + [3KBr.nH_2O](l) \qquad -76.0 \text{ kcal mol}^{-1} \Big) \text{(ii)}$$

$$AlI_3(c) + [3KCl.nH_2O](l) \qquad -89.1 \text{ kcal mol}^{-1} \Big) \text{ (i)}$$

$$AlCl_3(c) + [3KI.nH_2O](l) \qquad -76.6 \text{ kcal mol}^{-1} \Big)\text{(ii)}$$
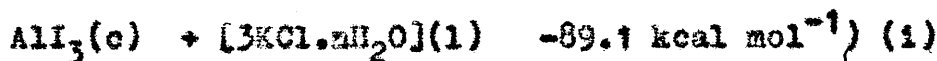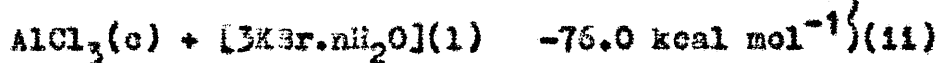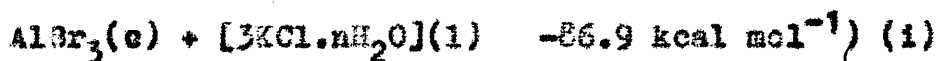
where n = ca 1000. From these results, using the value for
ΔH_f^O $AlCl_3(c)$ from Gross and Hayman[94], and assuming (after
Berthelot) that the resultant solutions for each pair (i) and
(ii) are identical,

$$\Delta H_f \ AlBr_3(c) = \Delta H(ii) - \Delta H(i) + 3 \ [\Delta H_f KBr(aq) -$$
$$\Delta H_f \ KCl(aq)] + \Delta H_f^O \ AlCl_3(c)$$

and similarly for aluminium iodide.

(c) Klemm and Tanke measured the enthalpies of solution; ΔH sol[n].

$AlCl_3(c) + [3KCl.n \; 100HCl](l) \quad -71.7 \; kcal \; mol^{-1}$

$AlCl_3(c) + [3KBr.n \; 100HCl](l) \quad -71.8 \; kcal \; mol^{-1}$

$AlCl_3(c) + [3KI.n \; 100HCl](l) \quad -72.3 \; kcal \; mol^{-1}$

$AlBr_3(c) + [3KCl.n \; 100HCl](l) \quad -85.5 \; kcal \; mol^{-1}$

$AlI_3(c) + [3KCl.n \; 100HCl](l) \quad -89.9 \; kcal \; mol^{-1}$

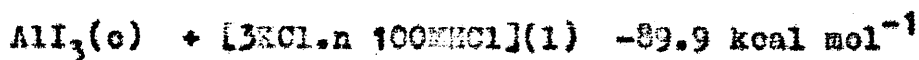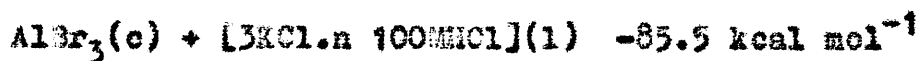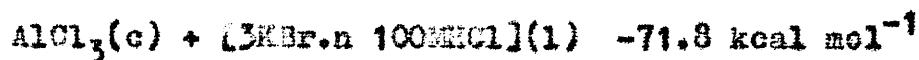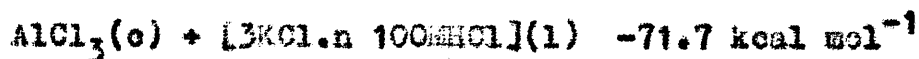where n represents a large, unspecified, excess. Using literature values[90] for the enthalpy of reaction

$$Al(c) + [n \; 100HCl](l) \xrightarrow[\Delta H \; Al]{} [AlCl_3(n-3)100HCl](l) + \tfrac{3}{2} H_2(g)$$

they obtained ΔH_f AlX_3 as

$$\Delta H_f AlX_3(c) = \Delta H \; soln. + \Delta H_{Al} - 3 \; \Delta H_f HCl(aq)$$
$$-3\Delta H_f \; KX(aq) + 3\Delta H_f \; KCl(aq)$$
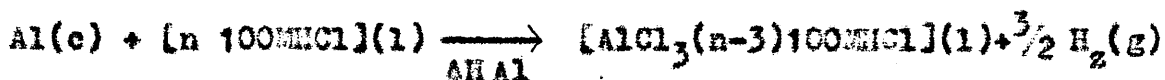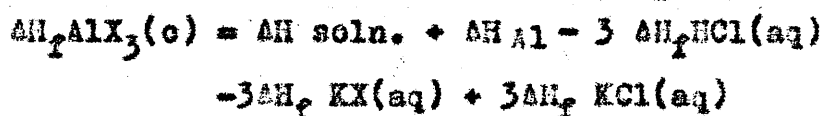
(d) Siemonsen used solution calorimetry similar to (c).

(e) Dear and Eley measured the enthalpy of solution of aluminium iodide in water $[-91.4 \pm 1.5 \; kcal \; mol^{-1}]$, then followed the same procedure as in (a).

(f) Corbett and Gregory measured the enthalpy of reaction

$$AlI_3(c) + 3HCl(g) \longrightarrow AlCl_3(c) + 3HI(g)$$
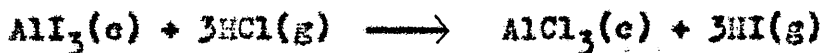
Knowing the other enthalpies of formation, $\Delta H_f^o AlI_3(c)$ was evaluated.

(g) Coughlin measured the enthalpy of solution of aluminium
chloride and aluminium in 4M hydrochloric acid, similar to (c).

(h) Gross and Hayman used combustion calorimetry to measure
directly the enthalpy of formation of aluminium chloride

$$Al(c) + \tfrac{3}{2} Cl_2(g) \longrightarrow AlCl_3(c)$$

Despite the seeming measure of agreement, there are
several reasons why many of the values are open to doubt:

(1) On dissolving aluminium halides in water or acid,
hydrolysis results in the formation of considerable acid mist
above the solutions, this being more marked for the bromide
and iodide than the chloride (see references 87 and 88).
This is bound to affect the accuracy of calorimetric results,
especially early work where only one or two experiments were
performed by each worker to determine enthalpies of solution.

(2) The hydrolysis, particularly for the bromide and iodide,
is slow[55] (see also Part Two, p. 61), while all the calcul-
ations assume that the final state is attained almost instant-
aneously.

(3) The enthalpy of hydrolysis might be expected to depend
on the aluminium halide to water ratio. Indeed, for aluminium
chloride, the enthalpy of dilution has been shown[97] to be
appreciable and negative over a large concentration range, due
to hydrolysis.   This is in contrast to most common electrol-
ytes, which have only small enthalpies of dilution, positive to

<u>ca</u> 1M, and negative in more dilute solution.

(4) The assumption is made in some methods that solution yields simple, aquated Al^{3+} and $3X^-$ ions. In fact, the situation is very complicated, for the nature of aluminium halides in solution is very sensitive to both pH and concentration changes, and the literature contains many papers postulating species such as $[Al(OH)(H_2O)_5]^{2+}$ (98, 99, 100, 106), $Al_2(OH)_5Cl$ (102), $[Al(H_2O)_n(OH)]_2^{4+}$ (101), $[Al(OH)Cl_2]_2$ (103) etc. in neutral or acid solution. Only for very dilute solutions at high or low pH does the situation seem at all clear-cut; for dilute solutions in strong acid (pH $\ll$ 2) the cation $Al(H_2O)_6^{3+}$ is predominant[100], while for dilute solutions in alkali (pH <u>ca</u> 13) the anion $Al(OH)_4^-$ is exclusively present[104, 105].

The relevance of these points can be demonstrated by comparing the literature values for the enthalpies of solution of aluminium halides in water (table 22).

For aluminium chloride, these values compare with an enthalpy of solution in 4.360M hydrochloric acid of -72.51 $\pm$ 0.05 kcal mol^{-1} (303K)[93], whereas for simple solution and complete dissociation to Al^{3+} + 3 Cl^-, the effect of the hydrochloric acid would be expected to be only slight.

TABLE 22

ENTHALPIES OF SOLUTION OF ALUMINIUM HALIDES IN WATER

AUTHORS	REFER- ENCE	$AlX_3 : H_2O$ MOLE RATIO	$-\Delta H$ SOLUTION (kcal mol^{-1})			TEMP K
			$AlCl_3$	$AlBr_3$	AlI_3	
Berthelot	87	ca 1000	76.3	85.3	89.0	282
Thomsen	107	1250	76.5	-	-	291
Roth and Buchner	108	2500-4730	78.1	-	-	293
Roth and Borger	109	4000-9000	79.5	-	-	293
Plotnikov and Yakubson	111, 110	2993	78.2	91.5	-	288
Dear and Eley	96	ca 10,000	-	-	91.4	298

It has also been shown[112] that the enthalpy of formation (and hence the enthalpy of solution) of aluminium chloride in hydrochloric acid is a linear function of the acid molality, with a spread of -7.6 kcal mol^{-1} from m = 0 to m = 5.

In view of the uncertainty, it was decided to redetermine the enthalpies of formation of aluminium bromide and iodide by measuring the enthalpies of solution in aqueous alkali, quantities not previously determined. The method used was to measure the enthalpy of solution of aluminium bromide (or iodide) in 0.1M sodium hydroxide solution containing sodium

chloride, and the enthalpy of solution of aluminium chloride
in alkali containing sodium bromide (or iodide)

(1) $AlX_3(c) + [nNaOH + 3NaCl](aq) \xrightarrow{\Delta H_1} [NaAl(OH)_4 + 3NaCl$
$+ 3NaX + (n-4)NaOH](aq)$

(2) $AlCl_3(c) + [nNaOH + 3NaX](aq) \xrightarrow{\Delta H_2} [NaAl(OH)_4 + 3NaCl$
$+ 3NaX + (n-4)NaOH](aq)$
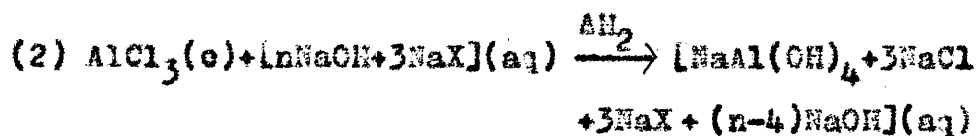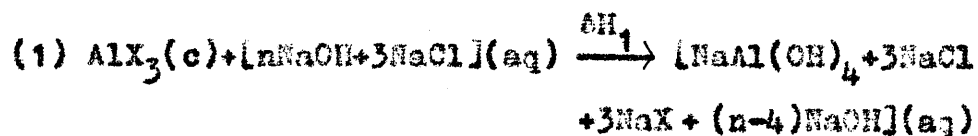
whence

$\Delta H_f^O AlX_3(c) = \Delta H_2 - \Delta H_1 + 3\Delta H_f^O NaX(aq) - 3\Delta H_f^O NaCl(aq)$
$+ \Delta H_f^O AlCl_3(c)$.

Besides the fact that aluminium is present in only one form,
this method has the advantage over other solution methods
that the acid mist formed above the solution is greatly
reduced.

EXPERIMENTAL

Chemicals

The same stocks of aluminium halides were used as described in Part Two (p. 65).

Analar grade (B.D.H. Ltd.) sodium chloride, sodium bromide and sodium iodide (stated purities 99.9%, 99% and 99.5% minimum respectively) were dried in an oven at $120°C$ before use.

0.100N sodium hydroxide (B.D.H. volumetric solution) was used directly.

Apparatus

Preliminary experiments showed the reactions to be extremely rapid, suited to constant-temperature-environment (CTE) calorimetry.

The calorimeter was an all-glass Dewar type (diagram 26), which has been used successfully in the Department for several years, and is fully described elsewhere[113,114]. Since a typical experiment involves long periods of waiting for equilibration, experiments were performed in overlapping pairs using two separate calorimeters. Minor modifications to the original design and the procedure for using the calorimeters are well described by Coley[115].

Temperature changes were monitored by an F53 thermistor (Standard Telephone and Cable Ltd.) connected as one arm of a

DIAGRAM 26   C.T.E. CALORIMETER
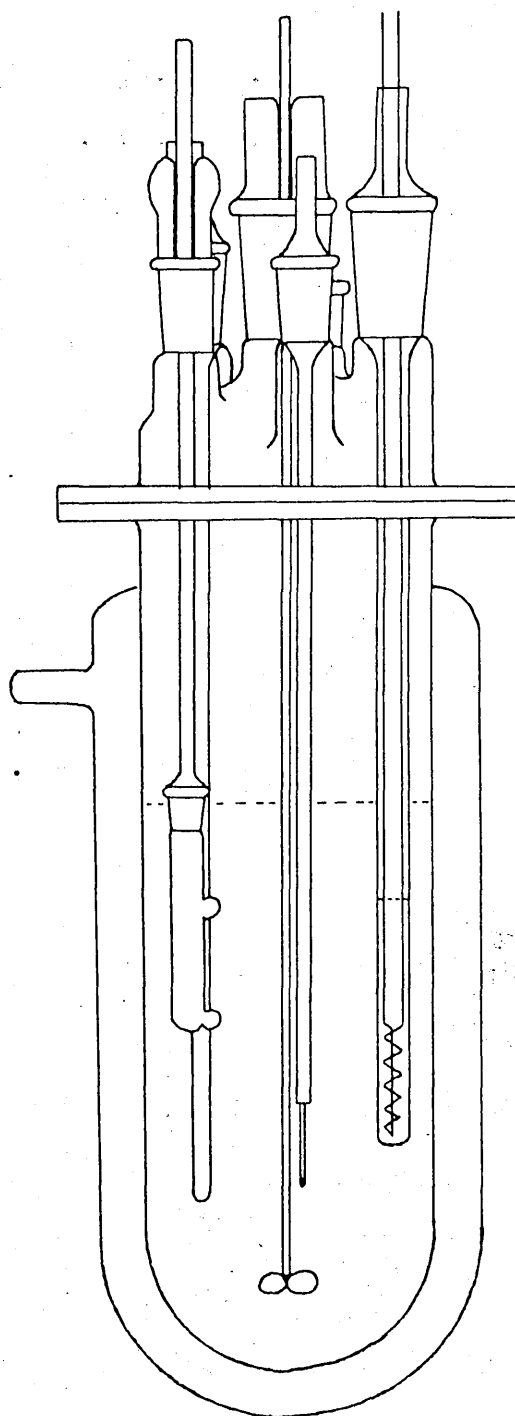
Wheatstone bridge, and with a resistance change of ca 180 Ω
per degree at 25°C. The only modification of Coley's
procedure[115] was that the out-of-balance bridge potential
was registered by a chart recorder (Bryans Ltd; model 27000)
in place of a galvanometer. It can readily be shown
(Appendix One, p. 187) that the displacement from zero shown
by the recorder is linear with respect to changes in thermistor
resistance, and by suitable adjustment of the recorder sensit-
ivity, resistances could be read off directly from a scale of
1 Ω ≡ 1 cm of chart paper.

The sample was contained in a thin-walled glass ampoule,
made with two small, very thin, glass bulbs, one above the
level of sample in the ampoule and one below, such that on
breaking the two bulbs calorimeter liquid could flow through
the ampoule to ensure complete mixing. The ampoule was filled
with aluminium halide in a dry-box, being weighed before and
after filling. The ampoule of aluminium halide was broken
into 200 ml of 0.100N sodium hydroxide containing sodium
chloride or sodium bromide (sodium iodide).

Calibration was achieved by an electric heater of
measured power (ca one watt), consisting of a spiral of wire
sited in a thin-walled glass well filled with light oil of
good thermal conductivity.

The system was returned to the bath temperature (25.00 ±
0.01°C) between reaction and calibration by the addition of

small pieces of solid carbon dioxide into the cooling tube.

Procedure

From Part Three, p. 110 ,

ΔH reaction $= \dfrac{f \times P \times t}{4184} \times \dfrac{M}{w} \times \dfrac{\ln R_1/R_2}{\ln R_3/R_4}$

$f = R_{obs.}/R_{exp.}$ to allow for resistance of leads

M = Molecular weight of sample.

w = Weight of sample used.

The resistance-time plots for pre- and post-reaction, and pre- and post-calibration, periods can be regarded as linear for times less than ca ten minutes (Appendix Two, p. 189).

As the reaction was quick (complete in under 0.5 min.), the values for the resistances before and after reaction, R_1 and R_2, could be obtained by extrapolating the straight fore- and after-periods to the time of ampoule breaking. In drawing the line for the after-period, the typical "overshoot" which occurred for ca one minute immediately following the reaction, was ignored. During this time, the system was not at equilibrium, the temperature of the calorimetric liquid being higher than that of the glass, due to the former being stirred and having a much better thermal capacity.

However, electrical heating during calibration took ca four minutes, and allowance had to be made for the heat lost during this period when extrapolating the fore- and after-

periods. This was achieved by Dickinson's "equal areas" method[115, 116, 117]. In the present circumstances, this is simplified by the linear form of the resistance-time plot during the heating period (ignoring the times needed for equilibration on switching the heater on and off, which are both small and also tend to cancel each other). R_3 and R_4 are obtained by extrapolating the fore- and after-periods to the time corresponding to the halfway point between the intersections of the linear heating period with the extended fore- and after-periods (see Appendix Three and diagram 27).

The performance of the two calorimeters was checked periodically using the enthalpy of neutralization of THAM, as described in Part Three, p. 107. The results were

1st Calorimeter		2nd Calorimeter	
Wt. THAM(g)	$-\Delta H$(kcal mol^{-1})	Wt. THAM(g)	$-\Delta H$(kcal mol^{-1})
1.1038	7.17	1.1870	7.17
1.0246	7.03	0.9289	7.10
1.0596	8.05	1.0770	7.18
1.0757	7.08	1.0418	7.07
1.0567	7.11	0.8324	7.10
1.0554	7.16	0.9954	7.11
0.9298	7.13	1.1229	7.13

Ignoring run 3 for set 1, which lies outside three standard deviations from the mean, this gives

1st Calorimeter	2nd Calorimeter
Mean = -7.11 kcal mol^{-1}	Mean = -7.12 kcal mol^{-1}
Standard deviation = 0.021	Standard deviation = 0.015
of the mean kcal mol^{-1}	of the mean kcal mol^{-1}

RESULTS

In all the reactions, the solid aluminium halide dissolved rapidly. In all cases, despite the alkali, some acid mist was formed above the solution in the calorimeter, this being most pronounced for aluminium bromide. However, the mist quickly dissolved, and had no apparent effect on the reaction trace. Analyses of the end products for halide confirmed that very little, if any, halide was lost.

$AlBr_3$ + NaOH/NaCl
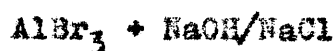
(i) Br (found) 1.46×10^{-3} g.atom   (ii) Br(found) 1.60×10^{-3} g. atom

    Br (calc) 1.47×10^{-3} g.atom   Br(calc) 1.62×10^{-3} g. atom

          99.3%   98.6%

AlI_3 + NaOH/NaCl

(i) I(found) 1.42×10^{-3} g.atom   (ii) I(found) 1.22×10^{-3} g. atom

    I(calc) 1.43×10^{-3} g.atom   I(calc) 1.23×10^{-3} g. atom

          99.3%   99.2%

$AlCl_3$ + NaOH/NaI

(i) Cl(found) 2.65×10^{-3} g.atom   (ii) Cl(found) 2.54×10^{-3} g. atom

    Cl(calc) 2.70×10^{-3} g.atom   Cl(calc) 2.56×10^{-3} g.atom

          98.1%   99.2%

The results are given in tables 23-26.

TABLE 23

ENTHALPY OF REACTION FOR

$$AlBr_3(c) + [nNaOH + 3NaCl](aq) \xrightarrow{\Delta H_R^o} [NaAl(OH)_4 + 3NaBr$$
$$+ 3NaCl + (n-4)NaOH](aq)$$
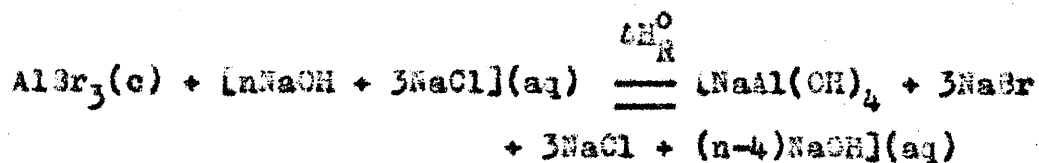
1st CALORIMETER			2nd CALORIMETER		
Wt. $AlBr_3$ g	n	$-\Delta H_R^o$ kcal mol^{-1}	Wt. $AlBr_3$ g	n	$-\Delta H_R^o$ kcal mol^{-1}
0.1119	47.7	93.03	0.0758	70.4	101.45
0.1336	38.5	101.47	0.1481	36.0	101.50
0.1756	30.4	100.85	0.1472	36.2	100.81
0.1728	30.9	102.78	0.1639	32.5	100.99
0.0907	58.8	101.48	0.1219	43.8	102.30
0.0886	60.2	102.33	0.1445	36.9	99.96
0.1308	40.8	101.57			

Run one in the 1st Calorimeter is greater than three standard deviations from the mean, and was hence ignored.

Mean = -101.46 kcal mol^{-1} [-424.50 kJ mol^{-1}]

Standard deviation of the mean $= \sqrt{\dfrac{6.39}{12 \times 11}}$ = 0.22 kcal mol^{-1}[0.92 kJ mol^{-1}]

Standard deviation from the mean $= \sqrt{\dfrac{6.39}{11}}$ = 0.77 kcal mol^{-1}[3.22 kJ mol^{-1}]
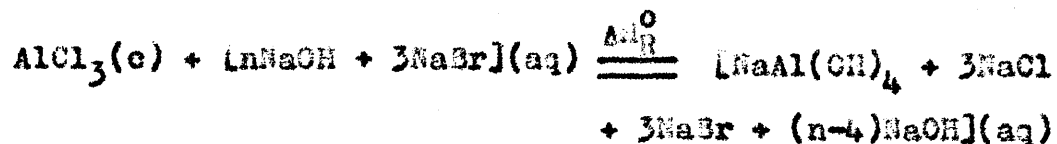
TABLE 24

ENTHALPY OF REACTION FOR

$$AlCl_3(c) + [nNaOH + 3NaBr](aq) \xrightarrow{\Delta H_R^0} [NaAl(OH)_4 + 3NaCl$$
$$+ 3NaBr + (n-4)NaOH](aq)$$

1st CALORIMETER			2nd CALORIMETER		
Wt. AlCl$_3$ g	n	$-\Delta H_R^0$ kcal mol^{-1}	Wt. AlCl$_3$ g	n	$-\Delta H_R^0$ kcal mol^{-1}
0.1175	22.7	83.82	0.0478	55.8	85.80
0.1090	24.5	85.36	0.0605	44.1	83.43
0.0916	29.1	83.70	0.1202	22.2	84.59
0.0602	44.3	84.87	0.0929	28.7	84.70
0.0831	32.1	83.54	0.0799	33.4	84.60
			0.1108	24.1	83.97

Mean = −84.40 kcal mol^{-1} [−353.14 kJ mol^{-1}]

Standard deviation
of the mean $= \sqrt{\dfrac{5.87}{11 \times 10}} = 0.23$ kcal mol^{-1} [0.96 kJ mol^{-1}]

Standard deviation
from the mean $= \sqrt{\dfrac{5.87}{10}} = 0.77$ kcal mol^{-1} [3.22 kJ mol^{-1}]

TABLE 25

ENTHALPY OF REACTION FOR

$$AlI_3(c) + [nNaOH+3NaCl]aq \xrightarrow{\Delta H_R^o} [NaAl(OH)_4+3NaI+3NaCl$$
$$+ (n-4)NaOH]aq$$
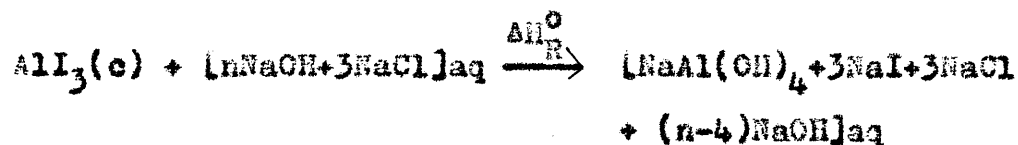
1st CALORIMETER			2nd CALORIMETER		
Wt. AlI$_3$ g	n	$-\Delta H_R^o$ kcal mol^{-1}	Wt. AlI$_3$ g	n	$-\Delta H_R^o$ kcal mol^{-1}
0.0753	108.3	106.30	0.3047	26.8	105.40
0.2527	32.3	106.14	0.3124	26.1	105.27
0.2735	29.8	106.49	0.1824	44.7	106.13
0.2351	34.7	105.67	0.2484	32.8	105.57
0.2340	34.8	106.18	0.1950	41.8	105.76
0.1680	48.5	105.88			

Mean = -105.89 kcal mol^{-1} [-443.04 kJ mol^{-1}]

Standard deviation of the mean $= \sqrt{\dfrac{1.525}{11 \times 10}} = 0.12$ kcal mol^{-1} [0.50 kJ mol^{-1}]

Standard deviation from the mean $= \sqrt{\dfrac{1.525}{10}} = 0.39$ kcal mol^{-1} [1.63 kJ mol^{-1}]

TABLE 26

ENTHALPY OF REACTION FOR

$$AlCl_3(c) + [nNaOH + 3NaI]aq \xrightarrow{\Delta H_R^o} [NaAl(OH)_4 + 3NaI + 3NaCl + (n-4)$$
$$NaOH]aq$$
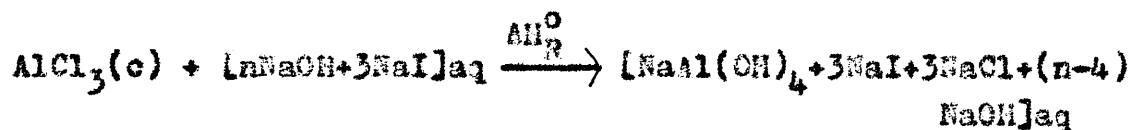
1st CALORIMETER			2nd CALORIMETER		
Wt. $AlCl_3$ g	n	$-\Delta H_R$ kcal mol^{-1}	Wt. $AlCl_3$ g	n	$-\Delta H_R$ kcal mol^{-1}
0.0868	30.7	84.53	0.0533	50.0	82.57
0.0910	29.3	84.69	0.0743	35.9	85.25
0.0765	34.9	82.56	0.0958	27.8	83.04
0.1433	13.6	85.02	0.1164	22.9	84.28
0.1081	24.7	83.79	0.1295	20.6	84.92
0.1202	22.2	84.64	0.1139	23.4	84.95

Mean = -84.19 kcal mol^{-1} [-352.25 kJ mol^{-1}]

Standard deviation of the mean $= \sqrt{\dfrac{10.26}{12 \times 11}} = 0.28$ kcal mol^{-1} [1.17 kJ mol^{-1}]

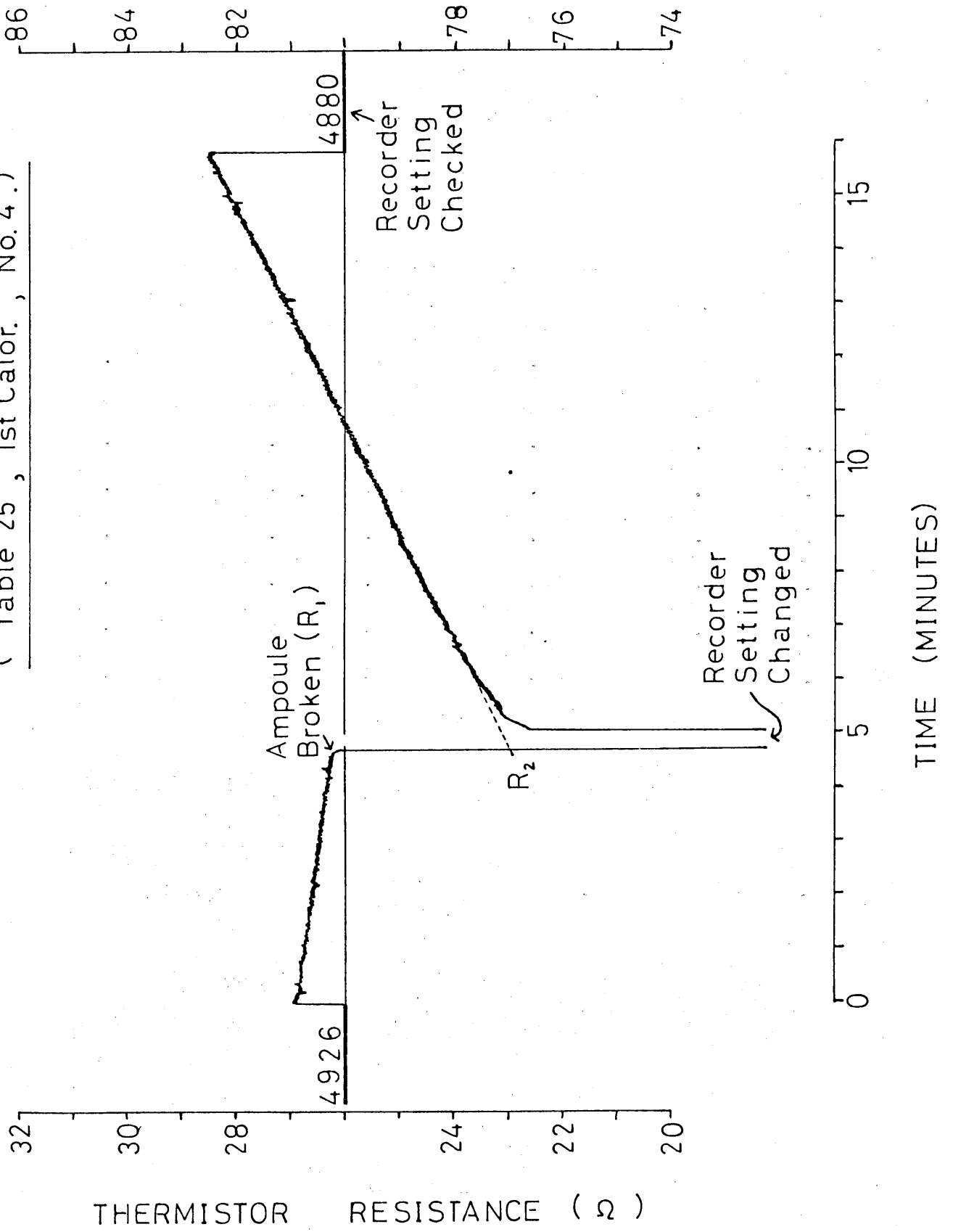Standard deviation from the mean $= \sqrt{\dfrac{10.26}{11}} = 0.97$ kcal mol^{-1} [4.04 kJ mol^{-1}]

DIAGRAM 27

TYPICAL Al X₂ REACTION TRACE

(Table 25 , 1st Calor. , No. 4.)

DIAGRAM 27 (CONT.)

Al X₃   CALIBRATION
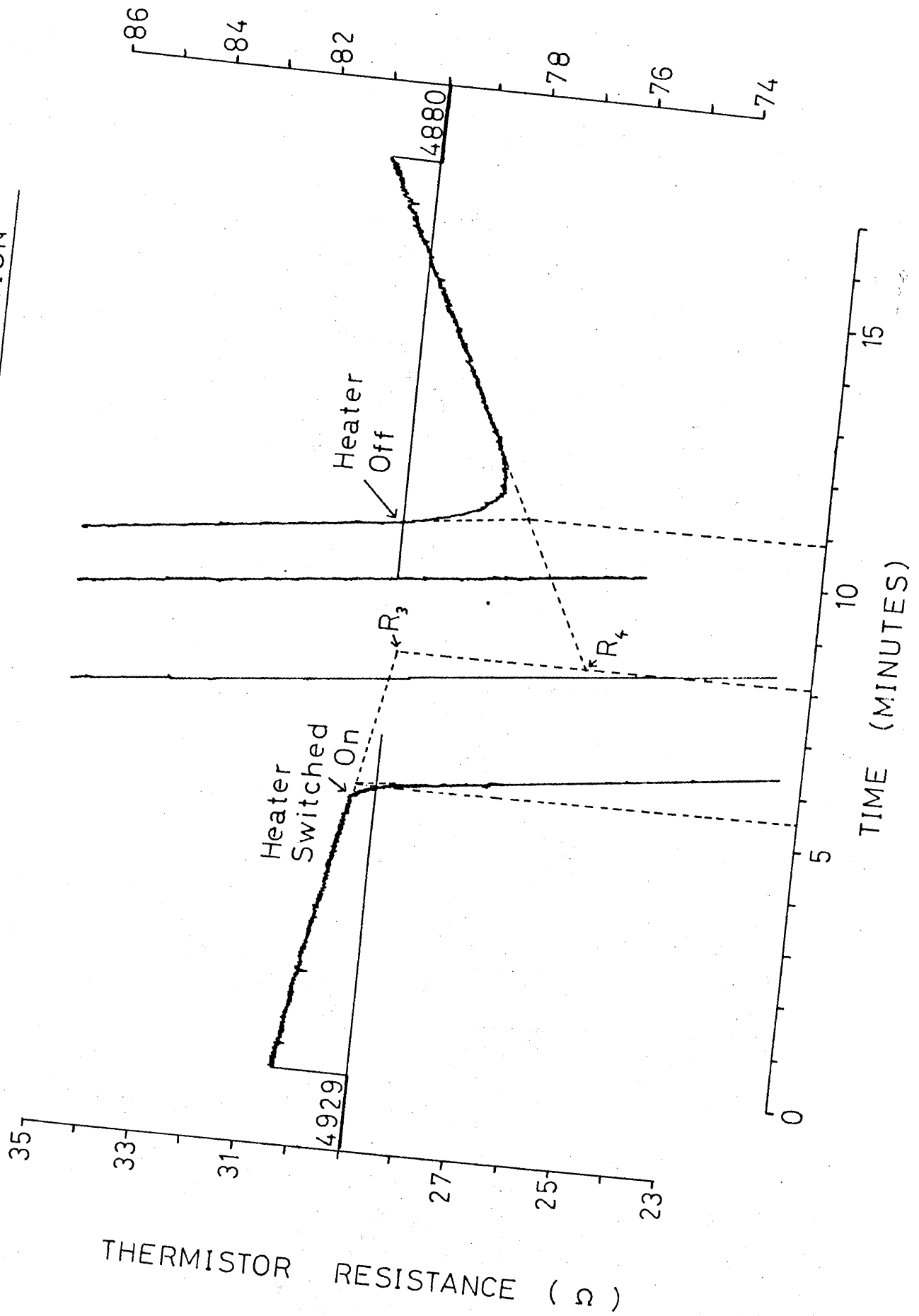
DISCUSSION

Enthalpy of Formation of Aluminium Halides

From the introduction,

$$\Delta H_f^o AlX_3(c) = \Delta H_R^o(2) - \Delta H_R^o(1) + 3\Delta H_f^o NaX(aq)$$

$$-3\Delta H_f^o NaCl(aq) + \Delta H_f^o AlCl_3(c)$$
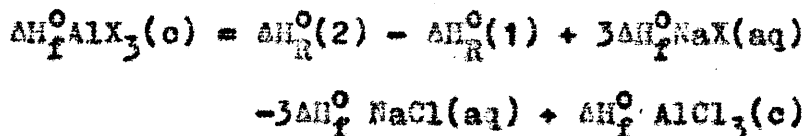
This ignores any contributions from

(i) Enthalpies of dilution arising from slight differences in concentration between the final products of reactions (1) and (2). The random spread of experimental results with regard to the weight of aluminium halide used shows these to be negligible.

(ii) Enthalpies of mixing of NaX(aq) + NaOH(aq) and NaCl(aq) + NaOH(aq). These too might be expected to be very small, and would tend to cancel each other.

The ancillary data used in the calculations were from reference 81 unless otherwise stated:

ΔH_f^o NaCl.7861H$_2$O $= -97.265$ kcal mol^{-1}

ΔH_f^o NaBr.6072H$_2$O $= -86.140$ kcal mol^{-1}

ΔH_f^o NaI.5259H$_2$O $= -70.610$ kcal mol^{-1}

ΔH_f^o AlCl$_3$(c) $= -168.80 \pm 0.20$ kcal mol^{-1} (from reference 94).
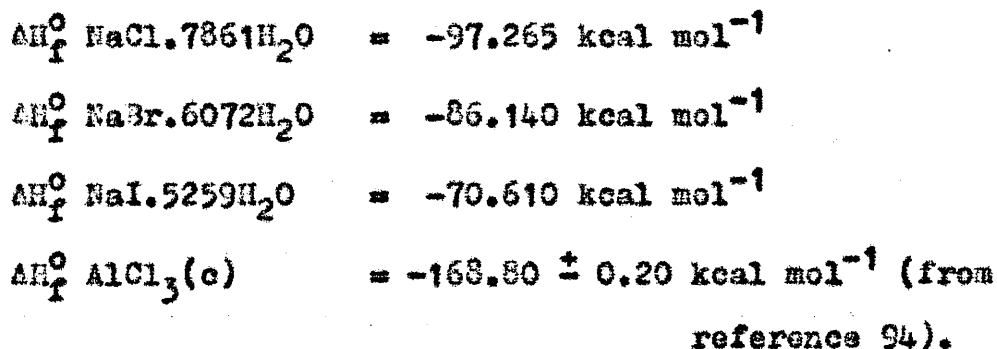
From which

$$\Delta H_f^O \ Al Br_3(c) = -118.4 \pm 0.6 \ kcal \ mol^{-1}$$

$$[-495.2 \pm 2.4 \ kJ \ mol^{-1}]$$

$$\Delta H_f^O \ AlI_3(c) = -67.1 \pm 0.6 \ kcal \ mol^{-1}$$

$$[-280.87 \pm 2.4 \ kJ \ mol^{-1}]$$

Enthalpy of Formation of Aqueous Sodium Aluminate

From the equation

$$AlCl_3(c)+[nNaOH+3NaX](aq) \xrightarrow{\Delta H_R^O(2)} [NaAl(OH)_4+3NaCl$$
$$+3NaX + (n-4)NaOH](aq)$$
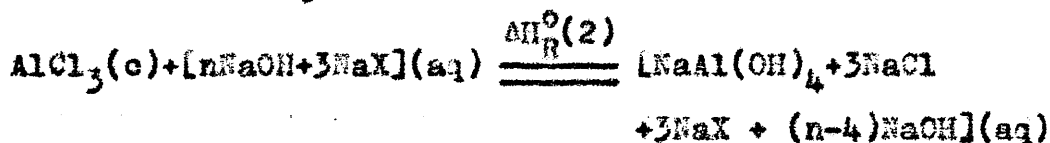
the standard enthalpy of formation of aqueous sodium aluminate
can be obtained as

$$\Delta H_f^O \ NaAl(OH)_4(aq) = \Delta H_R(2) + \Delta H_f^O AlCl_3(c) - 3\Delta H_f^O NaCl(aq)$$
$$+ 4\Delta H_f^O NaOH(aq)$$

Using the values given above in conjunction with

$$\Delta H_f^O \ NaOH.555H_2O = -112.12 \ kcal \ mol^{-1} \ (reference \ 81)$$

leads to a value of

$$\Delta H_f^O \ NaAl(OH)_4.15000 \ H_2O = -409.9 \pm 0.4 \ kcal \ mol^{-1}$$

$$[-1715.0 \pm 1.6 \ kJ \ mol^{-1}]$$

This compares with the value obtained from references 71
and 81 (origin not given) by adding $\Delta H_f^O \ Na^+(aq) + \Delta H_f^O Al(OH)_4^-(aq)$
both at unit molality, of

$$\Delta H_f^O \ NaAl(OH)_4.55.6H_2O = -413.5 \ kcal \ mol^{-1}$$

$$[-1730.0 \ kJ \ mol^{-1}]$$

PART FIVE

THE PHOSPHORYL CHLORIDE

- BORON TRICHLORIDE COMPLEX

INTRODUCTION

Although easily prepared and handled, the 1:1 complex between phosphoryl chloride and boron trichloride has been the source of much controversy in recent years, on two main fronts:

(1) The nature and interpretation of its infra-red spectrum

(2) The value for the enthalpy of dissociation,

$$POCl_3 \cdot BCl_3(c) \rightleftharpoons POCl_3(g) + BCl_3(g).$$
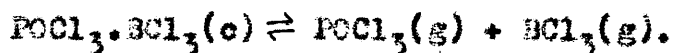
(1) INFRA-RED SPECTRUM AND INTERPRETATION

Four possible structures could be conceived for the adduct:

(a) Coordination through oxygen to boron, $Cl_3PO \rightarrow BCl_3$

(b) Coordination through chlorine to boron, $Cl_2PCl \rightarrow BCl_3$
$$\underset{O}{\overset{\|}{Cl_2PCl}} \rightarrow BCl_3$$

(c) As the extreme case of (b), an ionic structure involving the tetrachloroborate ion, $[POCl_2]^+ [BCl_4]^-$.

(d) A combination of ionic and dative covalent bonding, $[POCl_2 \cdot BCl_2]^+ Cl^-$

Examples of both (a)[118-121] and (b)[122,123] are described in the literature, while the BCl_4^- ion is also well documented[124]. Conductimetric[125] and ^{37}Cl-exchange[126] experiments have shown

that there is negligible ionization for solutions of the
complex in boron trichloride, while in phosphoryl chloride
solution there is appreciable ionization, the nature of which
is not yet certain. Although ionization to (c) is more
likely, (d) cannot be completely ruled out[125].

Certain predictions can be made[113,127,131] about the
shifts expected in the infra-red spectrum of (a), (b), (c) and
(d) relative to the frequencies in pure boron trichloride and
pure phosphoryl chloride. In (a), (b) and (c), but not (d),
the boron goes from sp^2 to sp^3 on complexing, which has the
consequence of lowering the B-Cl stretching frequencies
(995 cm^{-1} and 956 cm^{-1} in ^{10}B and ^{11}B boron trichloride
respectively for the asymmetric stretching mode). In case
(c), the characteristic BCl_4^- frequencies[124] should be
observed. With coordination through oxygen, as in (a) and
possibly (d), a considerable lowering of the P=O stretching
mode is expected (1290 cm^{-1} in phosphoryl chloride),
accompanied by a raising of the P-Cl stretching modes (595 cm^{-1}
(gas) or 581 cm^{-1} (liquid) for the asymmetric mode, 490 cm^{-1}
(gas) or 485 cm^{-1} (liquid) for the symmetric mode, in phosphoryl
chloride). For (b) and (c) the opposite should occur, with a
very slight increase in the P=O stretching mode, and a marked
decrease in the P-Cl frequencies, similar to the situation
occurring in the complexes of nitrosyl and acetyl halides[128].
With (a) and (b), vibrations associated with the newly formed

PO-B or PCl-B bonds are expected. However, these should be only weak if the pattern of other boron-oxygen complexes is followed.

Three main groups of workers have published the infrared spectrum of $POCl_3.BCl_3$. Waddington et.al.[121] used a nujol mull between sodium chloride or potassium bromide plates. They found a strong band at 1290 cm^{-1}, which they assigned to an unchanged P=O stretching frequency. Despite this, they postulated structure (a) on the basis of a weak band at 1190 cm^{-1}, which they assigned to a B-O stretching mode, and a large decrease in B-Cl stretching frequencies (700 cm^{-1} and 657 cm^{-1} for ^{10}B and ^{11}B). In a second paper[129], an additional weak band at 1150 cm^{-1} was assigned to an ^{11}B-O stretching mode, and the 1190 cm^{-1} band to ^{10}B-O. The bands assigned to P-Cl stretching modes showed only very slight frequency shifts.

Gerrard et.al.[130,131] also concluded from a nujol mull (potassium chloride plates) that the P=O stretching frequency was unchanged on complexing. This, together with the presence of what was termed a "BCl_4^- envelope" in the 700 cm^{-1} region led them to the conclusion that the ionic structure (c) was correct. They also claimed that a slight increase in the P-Cl stretching frequencies (588 cm^{-1} and 490 cm^{-1}) was compatible with a change in hybridization from tetrahedral $POCl_3$ to planar $POCl_2^+$. No trace was found of the 1190 cm^{-1}

or 1150 cm^{-1} bands assigned by Waddington to B-O stretching modes.

Goubeau et.al.[127] obtained the low-temperature infra-red spectrum and the room temperature Raman spectrum as part of a systematic investigation of $POX_3.MX_3$ complexes (X = halogen, M = B, Al, Ga or In). At low temperatures, no 1290 cm^{-1} band was found, but a strong band at 1157 cm^{-1} was attributed to a stretching mode of P=O in the adduct. Strong bands at 713 cm^{-1} and 382 cm^{-1} were assigned to B-O stretching and B-O-P bending modes respectively. The asymmetric B-Cl stretching modes were lowered to the region 727 - 795 cm^{-1}, while the asymmetric and symmetric P-Cl stretching modes showed a marked increase to 642 cm^{-1} and 505 cm^{-1} respectively. The room temperature Raman spectrum gave substantially analogous results. Goubeau concluded on the basis of these assignments that structure (a) was correct. He also stated, giving no details, that the conflicting results of Waddington and Gerrard were due to dissociation, hydrolysis and reaction with the cell windows.

In addition to the three main works mentioned, SenGupta[132] obtained the infra-red spectrum of the adduct in carbon disulphide and cyclohexane solutions, when the spectra compared in their salient features with those of Waddington, but not with those of Goubeau i.e. P=O stretching mode at 1300 cm^{-1}, B-O band at 1200 cm^{-1}.

The object of the present work was to try to resolve the

discrepancies between the various results, both by repeating some of the published work and by obtaining spectra using different experimental techniques.   The conditions employed were :-

(i) Gas phase infra-red.

(ii) Low temperature, solid phase infra-red.

(iii) Room temperature solid phase infra-red, obtained by subliming the adduct on to the windows of a gas cell.

(iv) Room temperature nujol mull.

(v) Room temperature solid phase Raman spectrum.

EXPERIMENTAL

Chemicals

Commercial boron trichloride (B.D.H. Ltd; minimum stated purity 98%) and phosphoryl chloride (B.D.H. Ltd; minimum stated purity 98%) were both further purified by fractional vacuum distillation through $-45^{\circ}C$ (chlorobenzene slush bath) to $-94^{\circ}C$ (toluene slush bath).   The purity of samples of each were tested by chloride analysis (Volhard's method) following alkaline hydrolysis.

Results were

$POCl_3$

Cl (found) 68.9% by mass

Cl (calc) 69.3% by mass

BCl_3

Cl (found) 90.8% by mass

Cl (calc) 90.8% by mass

The 1:1 adduct was prepared by condensing an excess of boron trichloride on to phosphoryl chloride, allowing the two to mix at room temperature, then pumping off excess boron trichloride at $-45^\circ C$. A white solid remained. A sample of the adduct was analysed for chloride:-

Cl (found) 78.7% by mass

Cl (calc) 78.6% by mass.

Apparatus and Procedure

Gas phase spectra were obtained using the cell described previously (p.   ), fitted with potassium bromide windows. 1:1 mixtures of gaseous phosphoryl chloride and boron trichloride were obtained by utilizing the vapour above the solid complex. Using the grease-free vacuum line described earlier (p. 53; diagram 10), a sample of the solid complex was placed in the mixing vessel, the line evacuated, and then isolated from the pump. With the remainder of the line, apart from the gas cell, saturated with vapour from the complex, the tap on the mixing vessel was shut to isolate the solid. Vapour was then allowed to fill the gas cell. This procedure ensured that the vapour in the cell was below saturation pressure, to avoid any sudden, slight, local cooling leading to condensation on the cell windows.

Room temperature spectra of the sublimed solid complex were obtained by making intentional use of the condensation

problem mentioned above.   The gas cell was opened to vapour
from the solid complex, which was maintained by hand-heat at
a slightly higher temperature.   With the gas cell saturated
with vapour, the tap was shut, and the cell windows subjected
to a flow of slightly-cooled air, when a thin film of solid
condensed on the plates.   With practice, the thickness of the
film could be controlled by the degree of heating or cooling
applied.   After the spectrum had been run, the cell was
re-connected to the vacuum line, all volatile products pumped
off, and a further spectrum obtained.

Room temperature nujol mull spectra were obtained by
grinding a sample of the adduct with a little nujol (dried
over sodium wire) in a dry-box, and then spreading a thin
film of the mull between potassium bromide plates.   The
spectrum was run as quickly as possible after making the mull
(ca two minutes) and again periodically after leaving the
plates + mull open to the atmosphere.

The low temperature (ca $-100^{o}C$) spectra of the solid
were obtained using the apparatus described previously (p. 56),
by spraying vapour from the complex on to a liquid nitrogen-
cooled caesium iodide plate.

All the infra-red spectra were run on a Perkin Elmer 337
machine.

The Raman spectrum of a sample of the solid, contained in
a capillary tube, was obtained on a Carey 81 instrument
(6328$\overset{o}{A}$ exciting line).

RESULTS AND DISCUSSION

Table 27 compares the bands found in the various infra-
red spectra, including for reference some literature spectra.
In diagrams 28-35, the spectra are reproduced, in the region
1300-400 cm^{-1}, for the following systems:-

28 Phosphoryl chloride gas.

29 Boron trichloride gas.

30 1:1 gaseous mixture.

31 Solid adduct at low temperatures (ca -100°C).

32 Sublimed solid adduct at room temperature.

33 The cell windows after the solid in 32 had been pumped off.

34 Nujol mull.

35 The nujol mull in 34 after standing for 45 minutes.

The spectra of gaseous phosphoryl chloride and gaseous
boron trichloride agreed very well with published data
(references 139 and 140 respectively). The spectrum of the
gaseous mixture showed no deviations from a simple super-
imposition of the individual spectra, with no evidence for
association.

In contrast, the spectrum of a 1:1 solid mixture at
-100°C showed almost total association. The P=O stretching
mode of free phosphoryl chloride (1320 cm^{-1} in the gas,
1290 cm^{-1} in the liquid) was absent or very weak. (A weak
band was present at 1280 cm^{-1}, but since this coincides with
an overtone (2 x 635 cm^{-1}), it is impossible to say whether

DIAGRAM 28   INFRA-RED SPECTRUM OF POCl$_3$ (g)

TRANSMITTANCE %

WAVENUMBER CM^{-1}

100

50

1300   1100   900   700   500

155
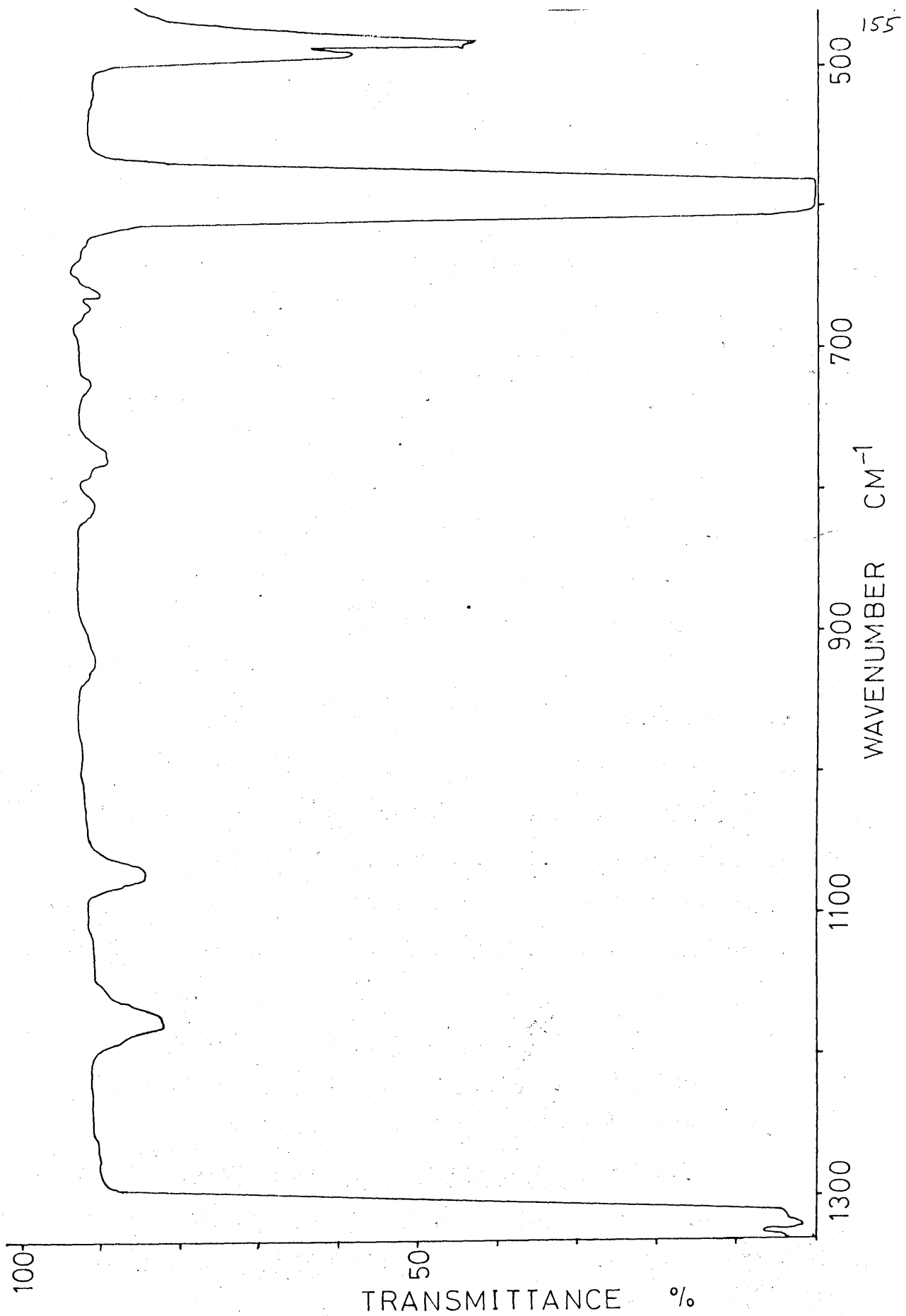
DIAGRAM 29

INFRA-RED SPECTRUM OF BCl$_3$ (g)

TRANSMITTANCE %

WAVENUMBER CM^{-1}

100

50

1100

900

700

500

156
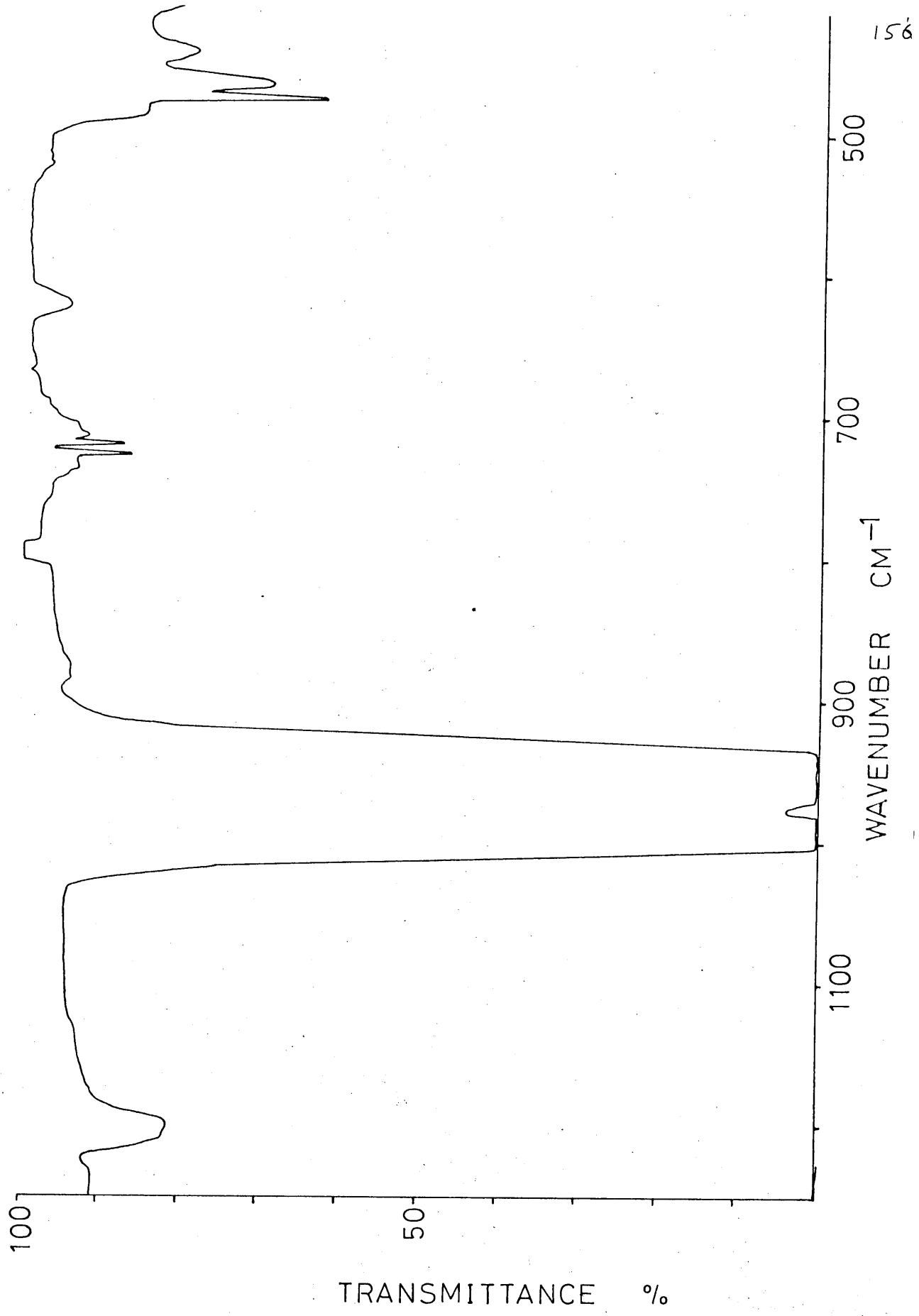
DIAGRAM 30   INFRA—RED SPECTRUM OF POCl$_3$ / BCl$_3$ (g)

157
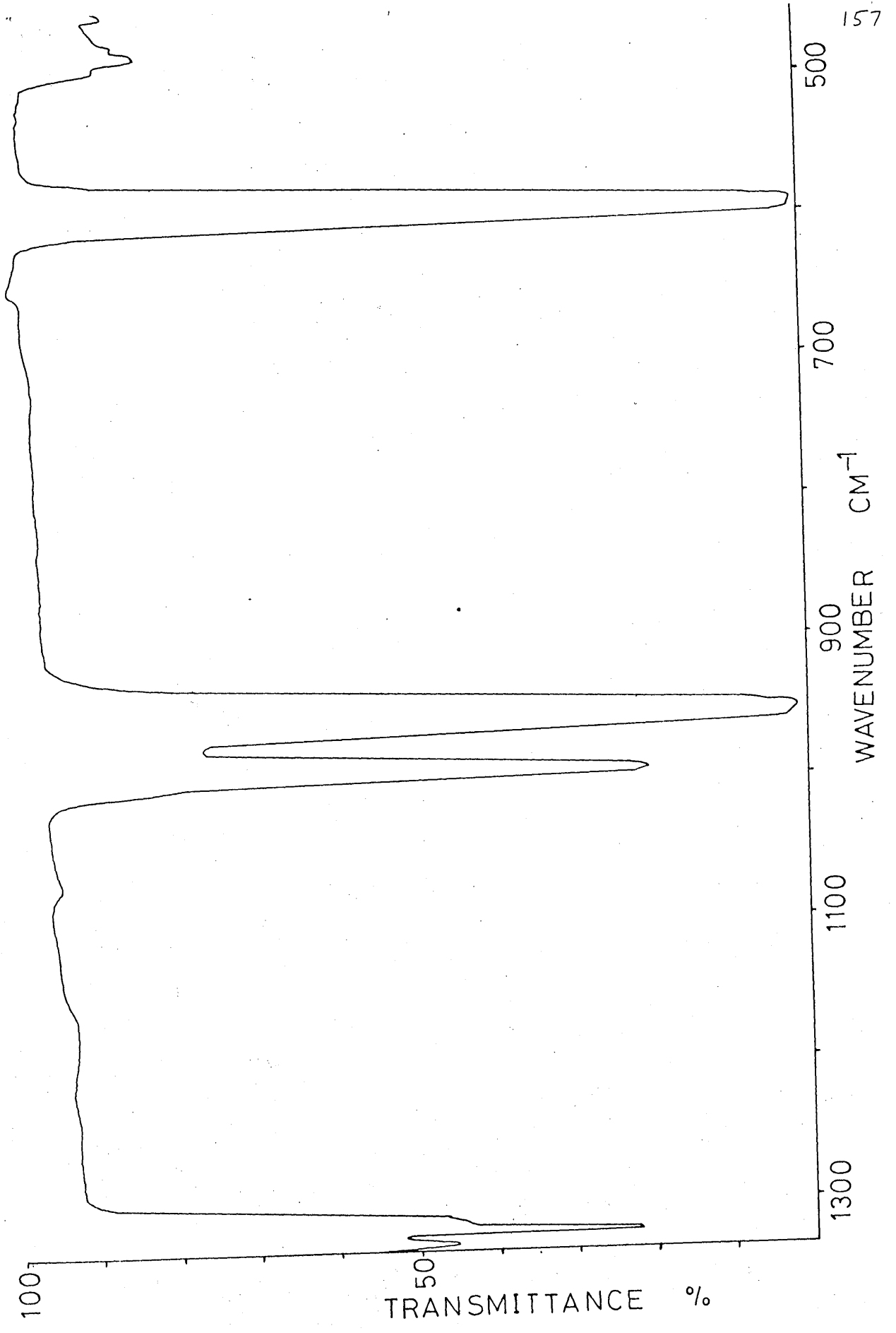
DIAGRAM 31

LOW TEMPERATURE INFRA-RED SPECTRUM

OF POCl₃.BCl₃ (s)

158
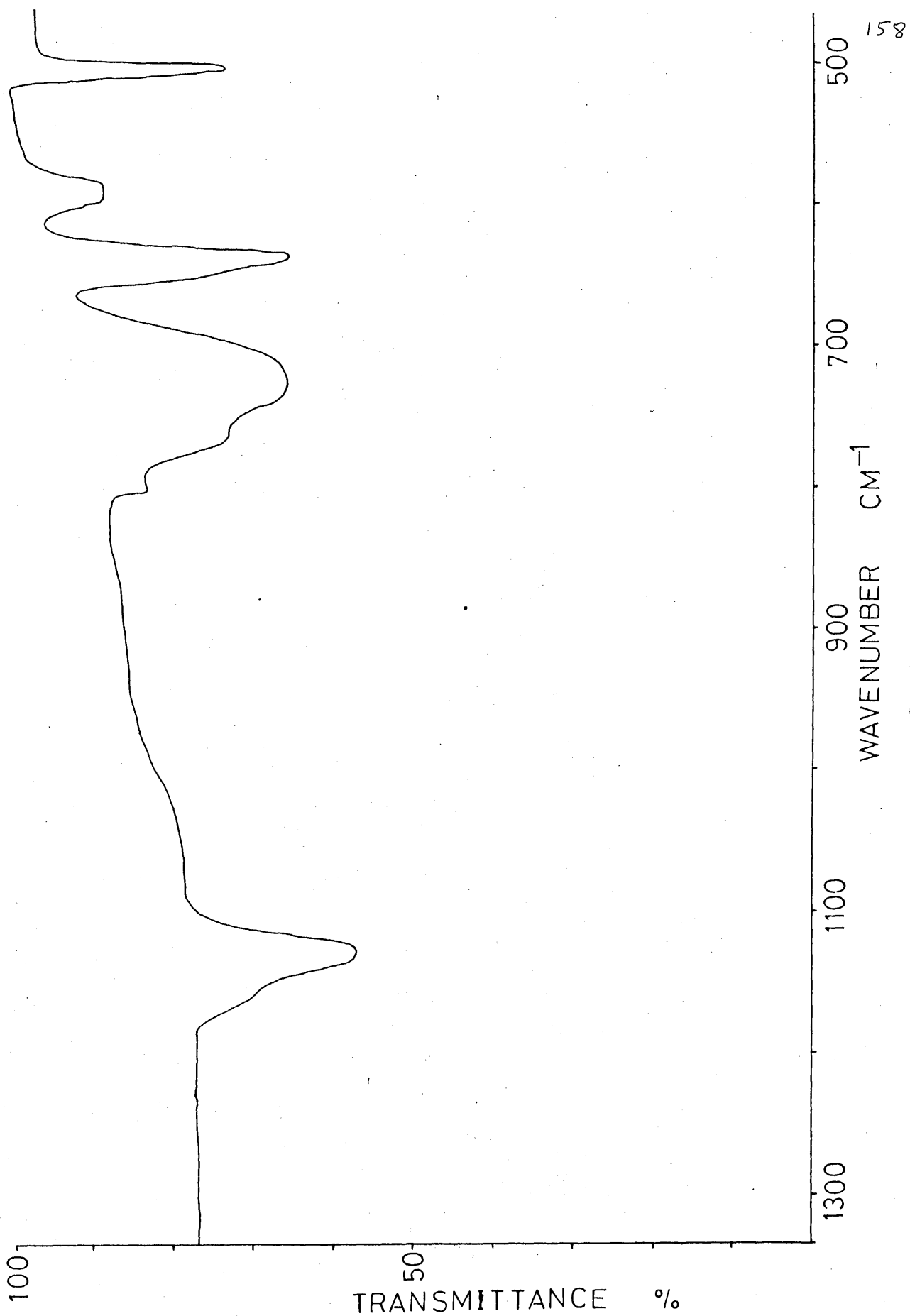
DIAGRAM 32   INFRA—RED SPECTRUM OF

POCl$_3$.BCl$_3$ (SUBLIMED SOLID)

159
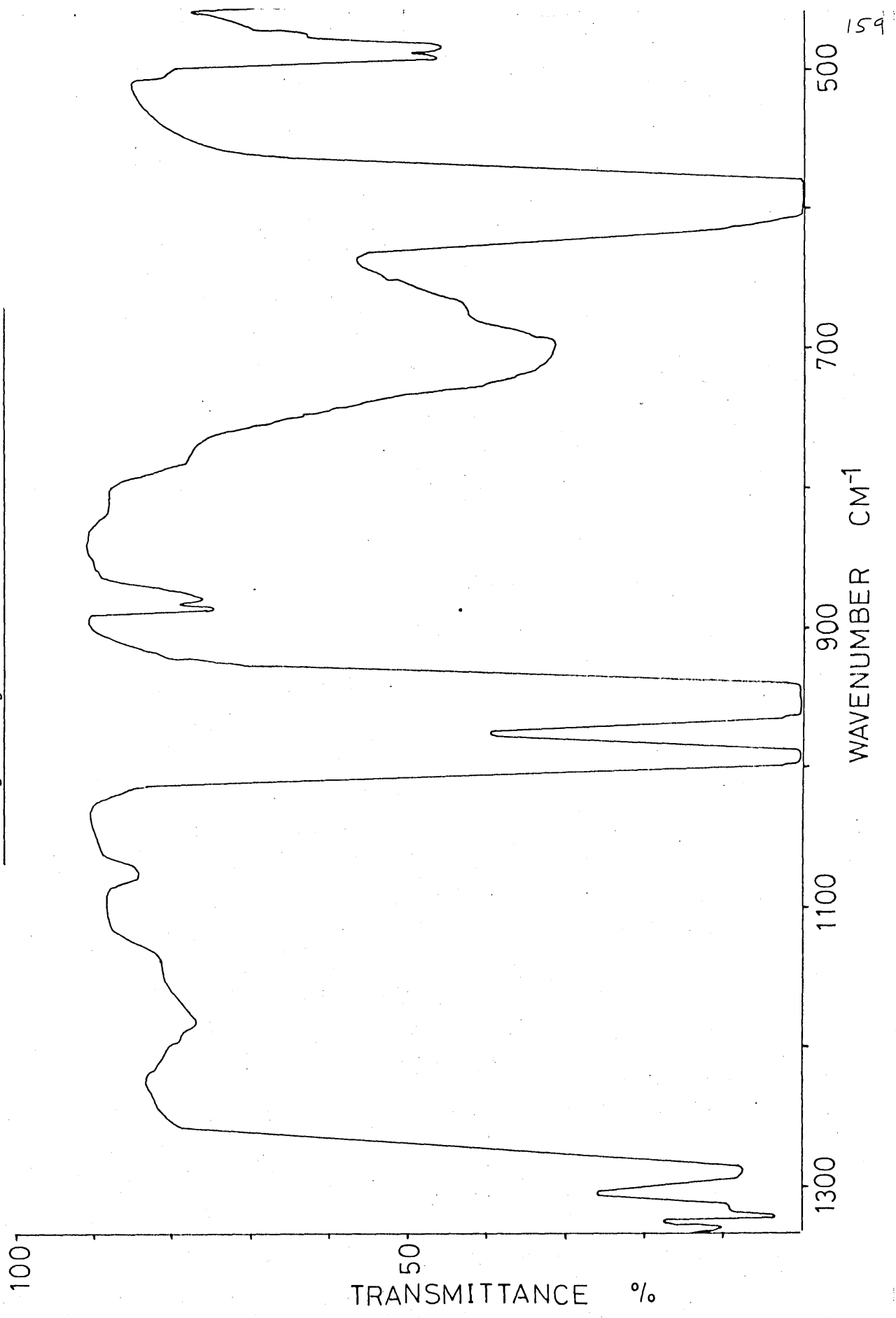
DIAGRAM 33

INFRA—RED SPECTRUM OF KBr WINDOWS USED
FOR DIAGRAM 32, AFTER PUMPING CELL

100

50

TRANSMITTANCE %

1300   1100   900   700   500

WAVENUMBER CM^{-1}

160
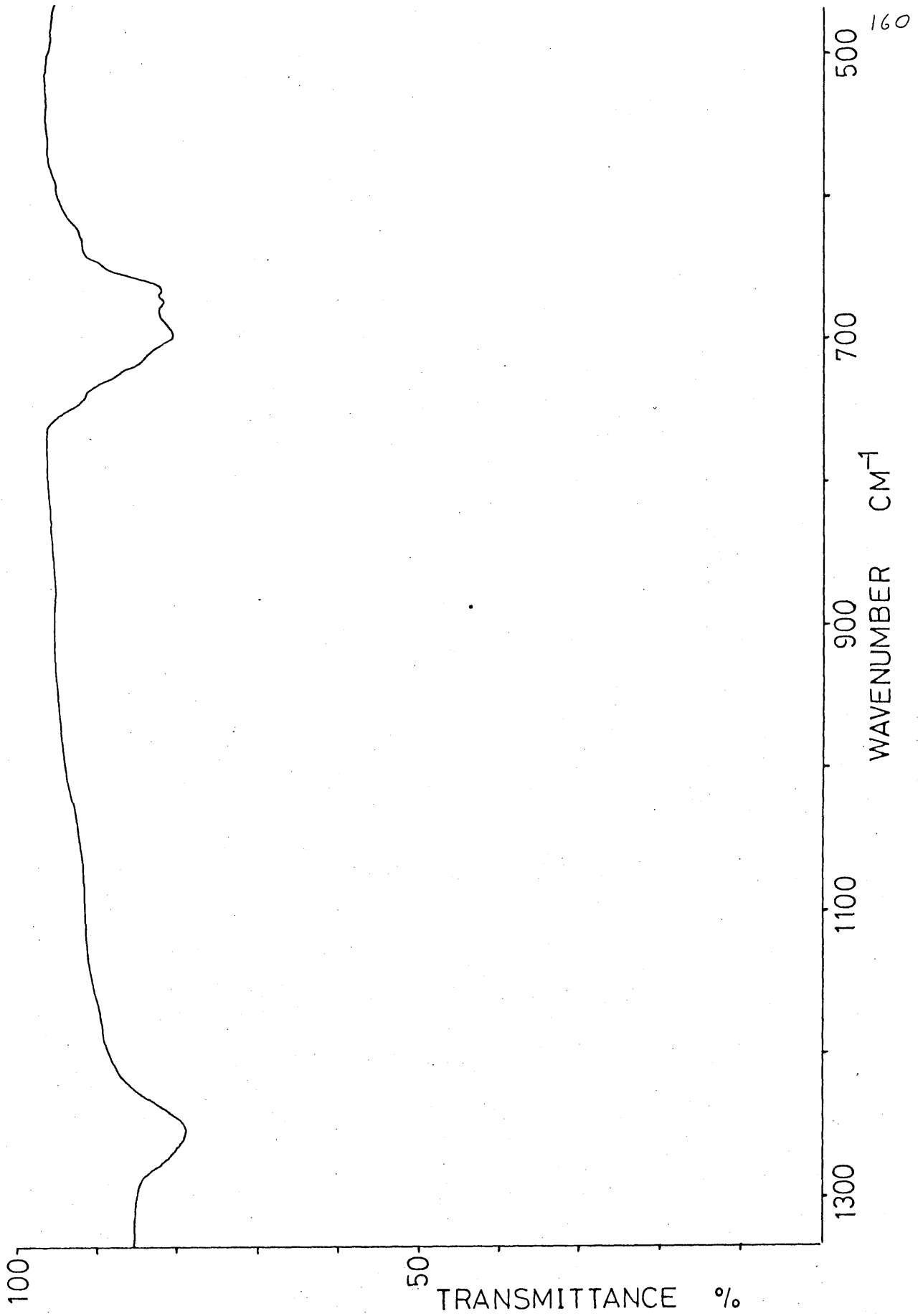
DIAGRAM 34   INFRA–RED SPECTRUM OF POCl$_3$.BCl$_3$ (NUJOL MULL)

←Nujol

WAVENUMBER CM^{-1}

500
700
900
1100
1300

TRANSMITTANCE %

100
50

161
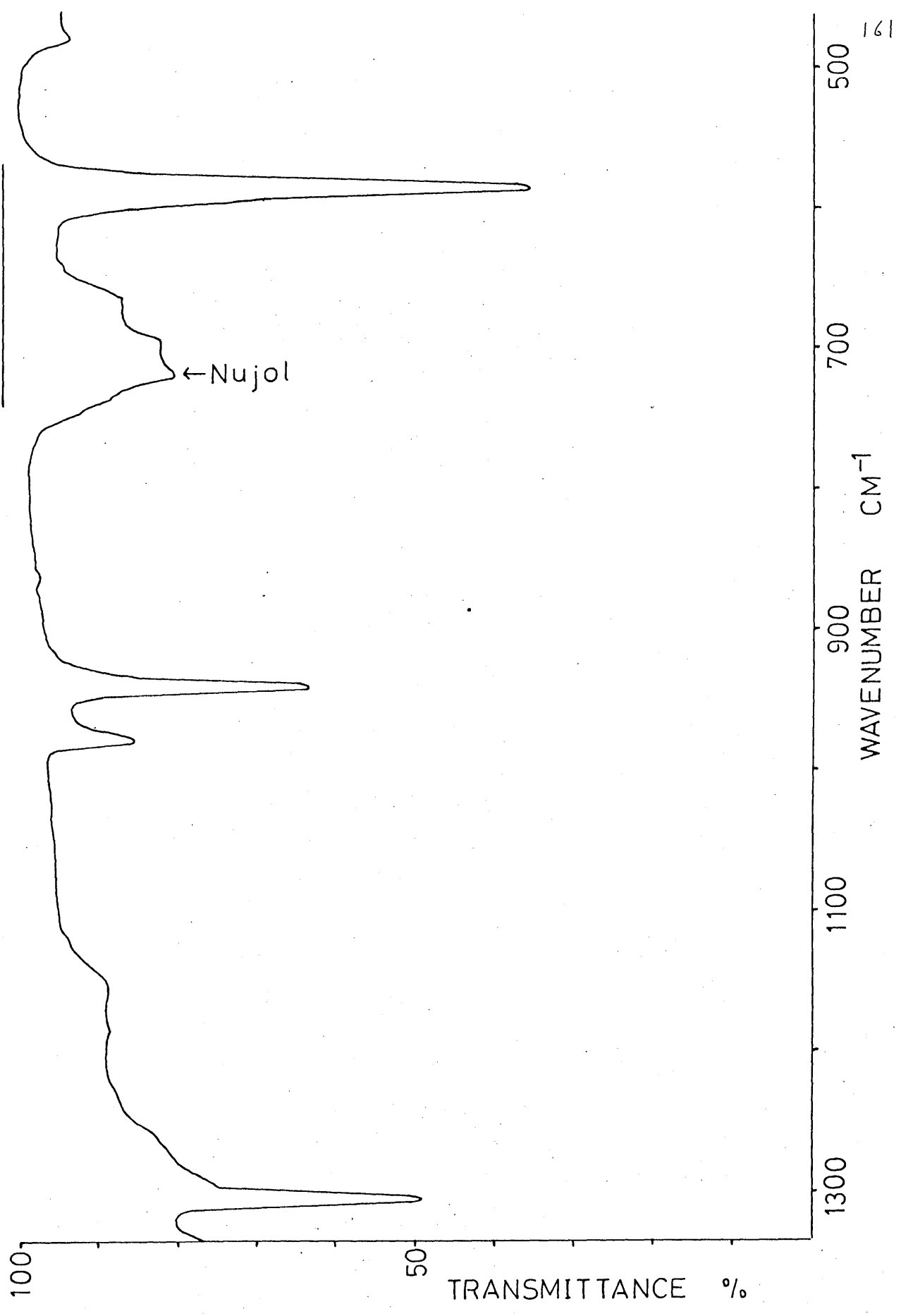
DIAGRAM 35

INFRA—RED SPECTRUM OF POCl$_3$.BCl$_3$ (NUJOL MULL)

AFTER STANDING FOR 45 MINUTES

TRANSMITTANCE %

100

50

1300 1100 900 700 500

WAVENUMBER CM^{-1}

16 α
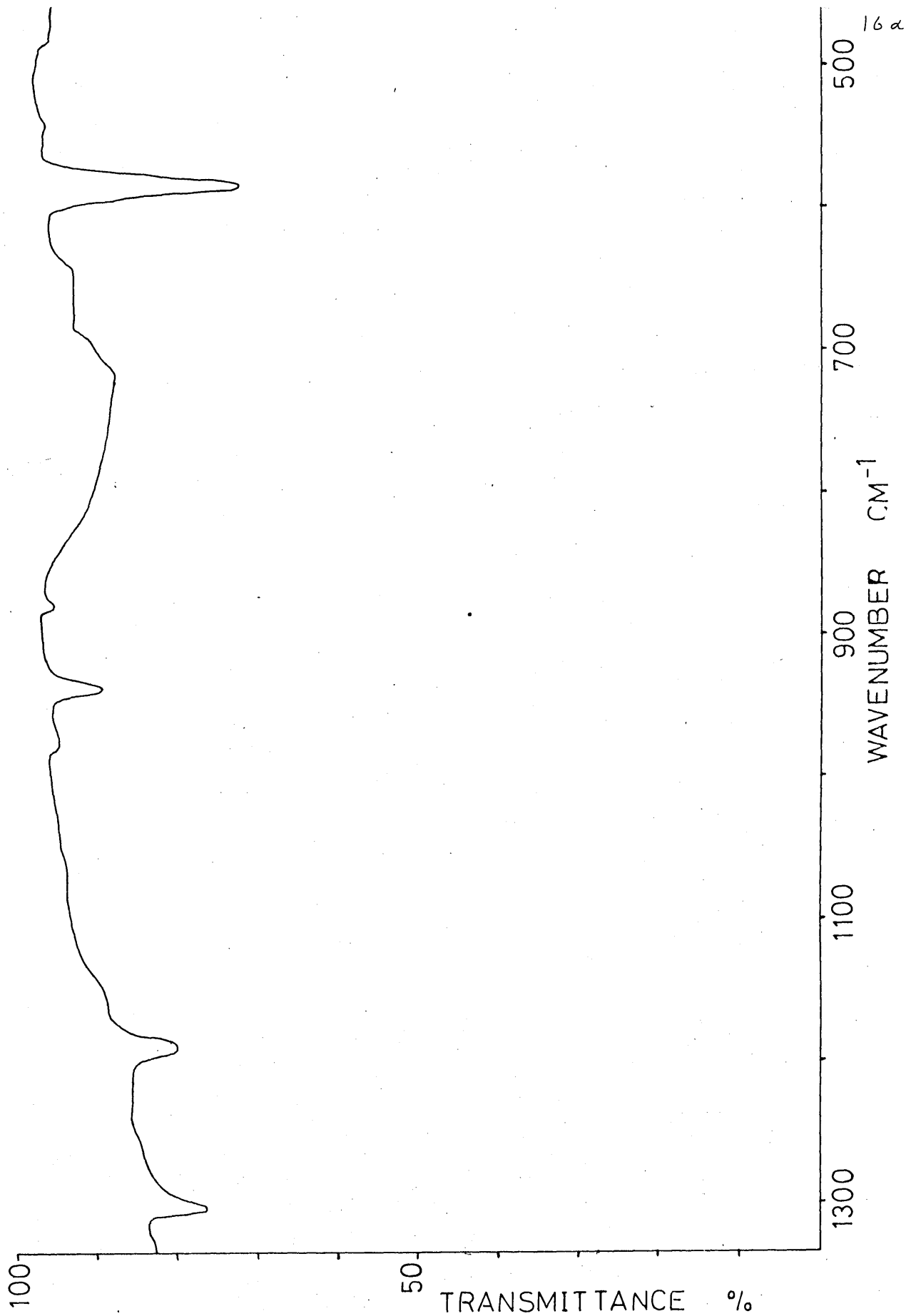
TABLE 27.   INFRA-RED SPECTRA

POCl$_3$ (g)	BCl$_3$ (g)	POCl$_3$ + BCl$_3$ (g)	POCl$_3$·BCl$_3$ LOW TEMPERATURE (s)	GOUBEAU, LOW TEMPERATURE (s)	SUBLIMED SOLID	SUBLIMED SOLID AFTER PUMPING	NUJOL MULL
2636 w		2636 w			2635vw		
			2240 vw				
	1990w	1990 w			1990 w		
	1920m	1920 m			1920 vw		
			1580 vw				
	1468w	1465 w			1465 vw		
	1430m	1422 m			1422 w		
	1385m	1390 m					
			1375 vw				
1320vs		1320 s			1320 s		
					1290 s		1305 s
			1280 vw				
					1260 sh	1260 m	
	1205 m						
1180 m		1180 m			1180 w		1180vw) 1180vw)
			1130 s	1167 s	1140 m		1140 w
1073 m		1070 m			1070 vw		
				1067 w			
			1020 vw				
	995vs	995 s			995 s		980 s
	955vs	955 s			955 s		940 s
920w							
			870 vw		880 m		870 vw
815 w							
			800 sh	795 sh			
730 w							

OF THE $POCl_3.BCl_3$ COMPLEX. (cm^{-1})

NUJOL MULL ON STANDING*	WADDINGTON (NUJOL MULL)*	GERRARD (NUJOL MULL)*	ASSIGNMENT
3200 s			O-H str. (hydrolysis)
			$2 \nu_2$(P=O str.) $POCl_3$(g)
			2(P=O str.) adduct
			$2 \nu_3$ (asy. str.) $^{10}BCl_3$
			$2 \nu_3$ (asy. str.) $^{11}BCl_3$
			2(B-Cl asy. str.) adduct
			$\nu_1 + \nu_3$ $^{10}BCl_3$(g)
			$\nu_1 + \nu_3$ $^{11}BCl_3$(g)
			$3 \nu_2$ $^{11}BCl_3$(g)
			ν_2(P=O str.) $POCl_3$(g) ?
1305 m	1290 s	1290 s	ν_2(P=O str.) $POCl_3$(l)
			2 (P-Cl asy. str.) adduct
			BCl_4^-
			$\nu_3 + \nu_4$ $^{11}BCl_3$
1190 m	1190 m		B-O str. (hydrolysis)
			$2 \nu_4$(P-Cl asy. str.) $POCl_3$(g)
1140 vw	1150 w		P=O str. adduct
			$\nu_1 + \nu_4$ $POCl_3$(g) ?
			2(P-Cl sy. str.) adduct
980 w	1010 m		ν_3(asy. str.) $^{10}BCl_3$(g) or (l)
940 m	975 m		ν_3(asy. str.) $^{11}BCl_3$(g) or (l)
	936 s		$\nu_4 + \nu_5$ $POCl_3$(g) ?
880 w			$\nu_1 + \nu_5$ $POCl_3$(g)
			adduct
			$\nu_4 + \nu_6$ $POCl_3$(g)

TABLE 27

POCl₃ (g)	BCl₃ (g)	POCl₃ + BCl₃ (g)	POCL₃.BCl₃ LOW TEMP-ERATURE (s)	GOUBEAU, LOW TEMP-ERATURE (s)	SUB-LIMED SOLID	SUB-LIMED SOLID AFTER PUMPING	NUJOL MULL*
			765 sh	765 sh	7)		)
				750 sh	700)		700)
			725 s	727 s	s(br))		s(br))
				713 sh	)		)
	728 w						
725vw							
	720 w						
					700)	700 m	700s(br)
					s(br))	670 m	670 s
670 w							
			635 s				
	620 w						
595 vs		595 s	590 m	595 w	590 s		585 s
		505 s		505 s	505 sh		
490 s		485 m)			490 m		480m)
	475 s	485 m)			475 m		480m)
	455 s	455 m			455 m		

s = strong intensity   v = very

m = medium intensity   br = broad

w = weak intensity   sh = shoulder

(CONTINUED)

NUJOL MULL ON STANDING[※]	WADDINGTON (NUJOL MULL)[※]	GERRARD (NUJOL MULL)[※]	ASSIGNMENT
	773 s		(B-Cl str.
	743 s		((+ B-O str. ?)
	715 s		(adduct
			$3\nu_4$ $^{11}BCl_3$(g)
			?
			$\nu_1 + \nu_4$ $^{11}BCl_3$(g)
700 m		700)	BCl_4^-
670 w	670 m	s(br))	BCl_4^-
			$2\nu_3$ $POCl_3$(g)
			(P-Cl asy. str.) adduct
			?
585 s	588 s	590 s	ν_4(P-Cl asy. str.)$POCl_3$(g)or(1)
			(P-Cl sy. str.) adduct
430 vw)	490 m)	490 m)	ν_1(P-Cl sy. str.)$POCl_3$(g)
480 vw)	490 m)	490 m)	ν_2 $^{10}BCl_3$(g)or(1) + $\nu_1 POCl_3$(1)
			ν_2 $^{11}BCl_3$(g) or (1)

) = only one band observed   asy. = asymmetric

※ = bands due to nujol omitted.   sy. = symmetric

str.= stretching mode   ? = not assignable

the free P=O stretching mode was totally absent; its
intensity was certainly greatly reduced]. In its place,
a new, strong, band appeared at 1130 cm^{-1}, attributable to
the stretching frequency of a P=O group acting as Lewis base.
In addition, the B-Cl asymmetric stretching modes (995 cm^{-1}
and 955 cm^{-1} in free $^{10}BCl_3$ and $^{11}BCl_3$) were shifted down to
the 800-700 cm^{-1} region, though the broad, ill-defined, nature
of the bands made precise assignments impossible. The P-Cl
asymmetric stretching mode increased from 595 cm^{-1} to 635 cm^{-1},
while the symmetric stretching mode also increased, from
490 cm^{-1} (gas) or 485 cm^{-1} (liquid) to 505 cm^{-1}. These
results agree well with those of Wertenberg and Goubeau[127],
the only discrepancies being that the complexed P=O mode
occurred ca 40 cm^{-1} lower (1130 cm^{-1}) than found by Goubeau
(1167 cm^{-1}), and there was no sign of the weak 1067 cm^{-1} band
found by Goubeau. In the present work, the bands were not
sharp enough to assign a B-O stretching mode (c.f. Goubeau
713 cm^{-1}). The shifts observed in the low-temperature spectrum
are compatible only with an oxygen-coordinated species,
structure (a).

The room temperature spectra of the adduct, both as
sublimed solid and nujol mull, were vastly more complicated
than those obtained at low temperatures. The solid film
spectrum in particular contained many more bands, some of which
were attributable to dissociated vapour, present in the cell as

a result of the technique used. The complexed P=O stretching mode (1140 cm^{-1}) was still present, though with a much reduced intensity compared to the low temperature spectrum. In addition, however, strong bands for free phosphoryl chloride were also observed (1320 cm^{-1} gas, and 1290 cm^{-1} liquid), suggesting a large degree of dissociation. This was confirmed by the presence of both complexed and free B-Cl stretching frequencies (ca 750 cm^{-1} and 995/955 cm^{-1} respectively). The complexed stretching modes slowly moved, with time, to lower frequencies ca 700 cm^{-1}. On attempting to pump all of the adduct out of the cell, all bands disappeared except for strong peaks at 700 cm^{-1} and 670 cm^{-1}, and a weaker peak at 1260 cm^{-1}, attributable to the BCl_4^- ion in $KBCl_4$[141]. This clearly demonstrates that reaction has occurred with the potassium bromide windows, a phenomonen which probably explains the "BCl_4^- envelope" of Gerrard et.al.[130,131]. The 1190 cm^{-1} assignment of a "B-O stretch" by Waddington et.al.[121,129] also could not be substantiated. Only a very weak band was found in this area, this being attributable to an overtone of free phosphoryl chloride (2 ν_4, P-Cl asymmetric stretching mode, 590 cm^{-1}). P-Cl symmetric stretching frequencies for both complexed and free phosphoryl chloride were present (505 cm^{-1} and 490 cm^{-1}), but for the asymmetric stretching modes, only the free band could be detected, (590 cm^{-1}), the complexed band (ca 640 cm^{-1}) being hidden. The only prominent feature

in the spectrum which could not be assigned was a B-type band of moderate intensity at 830 cm^{-1}. This had not been reported previously, and could not be assigned to any conceivable reaction products, such as free phosphoryl chloride, free boron trichloride, phosphoryl bromide, boron tribromide, tetrachloroborate, tetrabromoborate, phosphorus acids etc.

The nujol mull spectrum confirmed the findings of the solid film spectrum, the main difference lying in the much weaker relative intensities of the adduct bands and of the 830 cm^{-1} band. In addition, on standing, the very weak 1180 cm^{-1} band increased markedly in intensity, and shifted to 1190 cm^{-1}, accompanied by the appearance of new bands at 3200 cm^{-1} and 800 cm^{-1}, in the O-H stretching and bending regions. These observations together suggest hydrolysis, and the spectrum of boric acid, H_3BO_3, indeed contains strong bands at 3150 cm^{-1}, 1190 cm^{-1} and 800 cm^{-1}. The other main band, at 1428 cm^{-1}, would be obscured by nujol peaks. This leads to the possibility that some, at least, of the intensity of the 1190 cm^{-1} band of Waddington et.al. may have been due to a hydrolysis product most of the other hydrolysis product bands being obscured by stronger peaks.

Due to fluorescence, the room-temperature Raman spectrum of the solid adduct could not be obtained above <u>ca</u> 500 $cm.^{-1}$. The bands that were observed agreed with the Raman spectrum of Goubeau[127], as shown in Table 23.

TABLE 28

RAMAN SPECTRUM OF POCl$_3$, BCl$_3$

Present Work	Goubeau	POCl$_3$(1)[127,139]	BCl$_3$(1)[127]	Assignment
161s	170s	193s		
178w	-			
223s	225s		255s	B-Cl in-plane def.
265m	265w	267m		P-Cl$_3$ deform.
306m	306w	337s		
376s	382s			
443s	445s		472s	B-Cl sym. str.
505m	505s	486s		P-Cl sym. str.
	642s	581w		P-Cl asym. str.
	713m			B-O adduct
	727sh		958w	[11]B-Cl asym. str.
	750sh			
	765sh		996vw	[10]B-Cl asym. str.
	795sh			
	1167w	1300m		P-O str.

It appears that there is far less dissociation under the conditions required for the room-temperature Raman spectrum than for the corresponding infra-red spectra.

In conclusion, it may be stated that these results are only compatible with an adduct involving coordination through oxygen, but which is readily dissociated at ambient temperatures,

(2) DISSOCIATION OF POCl$_3$.BCl$_3$

Values for the enthalpy of dissociation

POCl$_3$.BCl$_3$(s) = POCl$_3$(g) + BCl$_3$(g) (ΔH diss.) can be derived

from three different sources:

(1) Burg and Ross[133] determined the vapour pressure-temperature

curve for the complex in the region 10-35°C from which, assuming

complete dissociation in the gas, they obtained

$$\log_{10} K_p = 15.803 - \frac{5714}{T}$$

Since

$$\frac{\Delta H^0}{RT^2} = \frac{d \ln K_p}{dT}$$

this gives

ΔH diss = 26.1 kcal mol^{-1} (109.2 kJ mol^{-1})

From vapour density measurements, it was calculated that the

vapour was at least 90% dissociated at a temperature (not

quoted) higher than for the pressure measurements.

(ii) Gutmann et.al.[134] measured the enthalpies of solution

in phosphoryl chloride, of boron trichloride and of the adduct

POCl$_3$.BCl$_3$, whence

BCl$_3$(l) + POCl$_3$(l) $\longrightarrow$ POCl$_3$.BCl$_3$(s)

$\Delta H = -7.9$ kcal mol^{-1} [-33.1 kJ mol^{-1}]
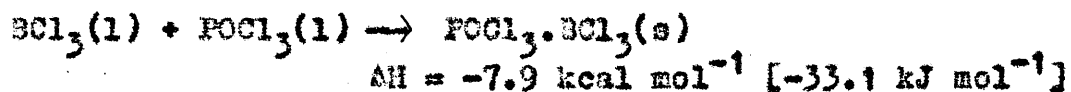
Using values from references 71 and 81 for the latent heats of

vaporization of boron trichloride and phosphoryl chloride

(5.6 and 9.2 kcal mol^{-1} respectively),

$\Delta H \, diss = 22.7 \; kcal \; mol^{-1} \; [95.0 \; kJ \; mol^{-1}]$

(iii) Finch, Gardner and Sen Gupta[132, 135] measured the enthalpy of hydrolysis of the adduct in water

$$POCl_3.BCl_3(s) + (n+6)H_2O(l) = [H_3PO_4 + H_3BO_3 + 6HCl + nH_2O](l)$$
$$\Delta H \; hyd.$$
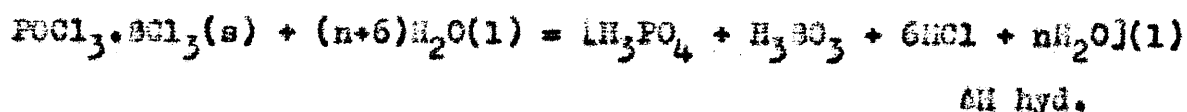
$\Delta H \; hyd = -123.2 \; kcal \; mol^{-1} \; [-515.6 \; kJ \; mol^{-1}]$

This leads to

$\Delta H_f^o \; POCl_3.BCl_3(s) = -271.2 \; kcal \; mol^{-1} \; [-1134.7 \; kJ \; mol^{-1}]$

and, using values[71,31] of

$\Delta H_f^o \; POCl_3(g) = -134.3 \; kcal \; mol^{-1}$

$\Delta H_f^o \; BCl_3(g) = -96.7 \; kcal \; mol^{-1}$

this gives

$\Delta H \; diss = 40.2 \; kcal \; mol^{-1} \; [-168.2 \; kJ \; mol^{-1}]$

Finch et.al.[132,135] confirmed this value by repeating their measurements with a fresh sample of adduct. Burg and Ross' values for the dissociation pressures were also confirmed, suggesting that the different values for the enthalpy of dissociation could not be attributed to differences between the samples of adduct used. It was postulated that one explanation for the discrepancies might be association in the gas phase at 298K, contrary to Burg's assumption i.e.

$$POCl_3.BCl_3(s) \rightleftharpoons POCl_3.BCl_3(g) \rightleftharpoons POCl_3(g) + BCl_3(g)$$
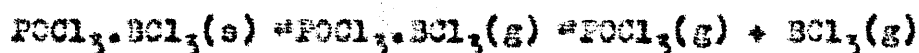
It was the object of the present work to test this postulate by measuring the association in mixtures of the two gases.

EXPERIMENTAL

Chemicals

The same sample of $POCl_3.BCl_3$ was used as for the spectroscopy (p. 151).

The water used for calibrating the pressure gauge was distilled from acid permanganate, and degassed by four trap-to-trap vacuum distillations.

The cyclohexane for testing the pressure gauge was a high purity sample (Phillips Petroleum Co. Ltd; stated minimum purity 99.99%), used directly after drying (grade 4A molecular sieves) and degassing.

Pure, distilled propionic anhydride (minimum purity 98%) was already available in the Department.

Apparatus and Procedure

Pressures were measured using a strain gauge (Bell and Howell Ltd; type 4-366). Pressures experienced by a thin, stainless steel, diaphragm were converted to a controlled strain in a Wheatstone bridge whose four arms consisted of strain gauge windings. A rod welded to the centre of the diaphragm transmitted its displacement to a spring element, the movement of which tilted two of the windings so as to increase their strain, and hence resistance, and the other two windings so as to decrease their strain and resistance. The system was arranged such that the output voltage of the out-of-balance Wheatstone bridge was a linear function of the applied

pressure.   The nominal 40mV full range output (0- ca 500 torr)
was amplified to ca 10V, giving 0.015 volts per torr.   The
voltage was registered on a digital voltmeter (Marconi Ltd;
TF 2600) reading correct to $\pm$ 1mV.

The pressure transducer was incorporated in the apparatus
shown in diagram 36.   The metal take-off from the transducer
was sealed into glass tubing of slightly wider diameter using
Torrseal resin (Varian Ltd.).   The apparatus was fitted with
a greaseless tap and joint for connection to the vacuum line.
The volume of the apparatus up to the seating of the tap was
determined as 561.2 and $\pm$ 0.1 ml by filling with water from a
burette and pipette.

In use, the apparatus was immersed, to the level of the
top of the transducer, in a water jacket which could be
thermostatted to $\pm$ 0.1^{o}C.   Readings could be taken in the
range 0-60°C.   When taking a series of measurements over a
wide range of temperatures, care had to be exercised that the
tap maintained a good seal at its lower seating.   Since the
coefficient of thermal expansion is much greater for Teflon
than glass, on cooling there was a tendency for leaking, while
at higher temperatures there was a danger that undue force
might crack the tap.

The thermal characteristics of the apparatus were deter-
mined in the form of a voltage-temperature graph, after
evacuating the vessel to 10^{-4} torr (i.e. effectively zero

DIAGRAM   36   PRESSURE—MEASURING   APPARATUS

To Vacuum
Line

Greaseless
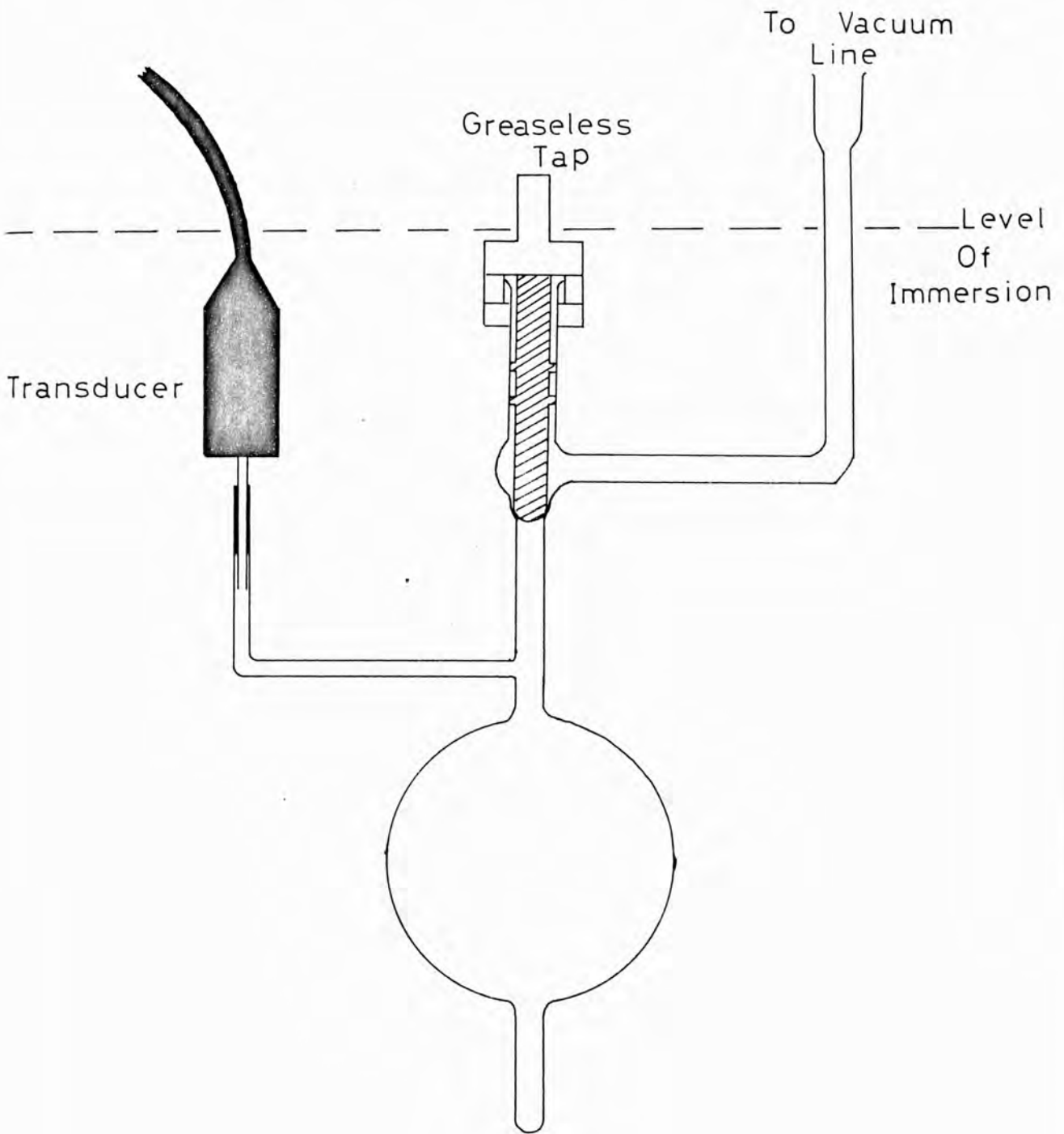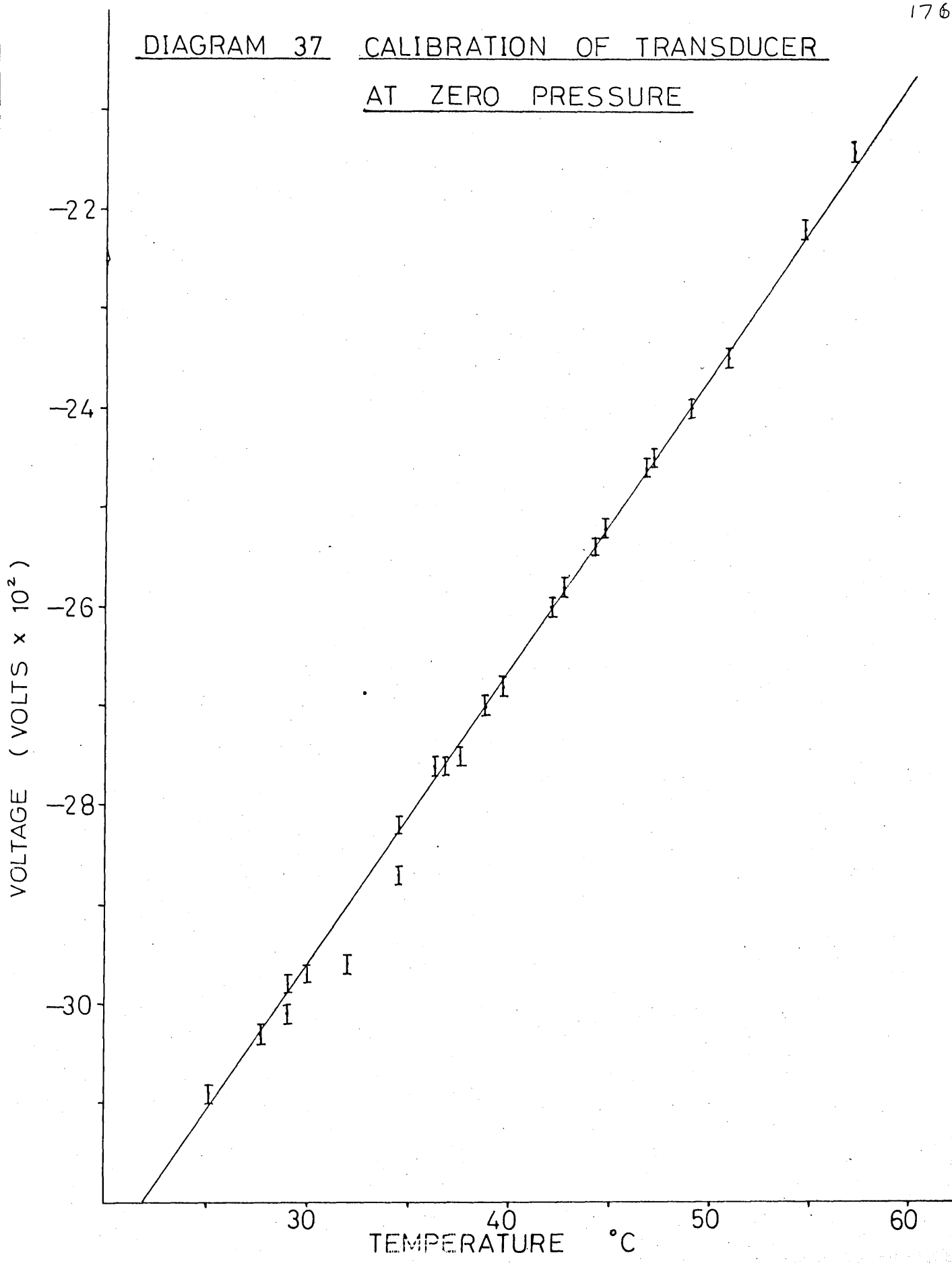Tap

Level
Of
Immersion

Transducer

DIAGRAM 37   CALIBRATION OF TRANSDUCER
AT ZERO PRESSURE

pressure). Diagram 37 shows this to approximate to a straight line in the range 25-55°C, with a slope of 0.0030V per degree. A mishap to the apparatus at a later stage necessitated repeating this determination, when readings taken over a wider temperature range (0-60°C) showed the graph to be an extremely gentle curve, approximating to a straight line for smaller temperature ranges. These graphs were used to compensate all measurements for thermal dependence of the voltage by arbitrarily selecting the 25.0°C value as a standard, and correcting voltage readings at other temperatures to 25°C.

The corrected voltage output from the transducer was calibrated in terms of pressure by using water as a standard[4,136]. The corrected voltage-pressure calibration graph is shown in diagram 38 for the region 0-100 torr. This line can be fitted to the equation

$$P = [70.373V + 21.78] \pm 0.07$$

where P = Pressure in torr $\pm$ 0.07 torr.

V = Corrected voltage in volts.

To test the accuracy of the system, the vapour pressure-temperature curve for cyclohexane was determined in the range 25-40°C (100-200 torr). Cyclohexane has often been suggested as a standard for pressure measurements[137], and its vapour pressure has been carefully studied[137]. The experimental points are plotted on the same graph as the literature curve in diagram 39.

CALIBRATION OF PRESSURE-MEASURING

APPARATUS WITH WATER

DIAGRAM 38
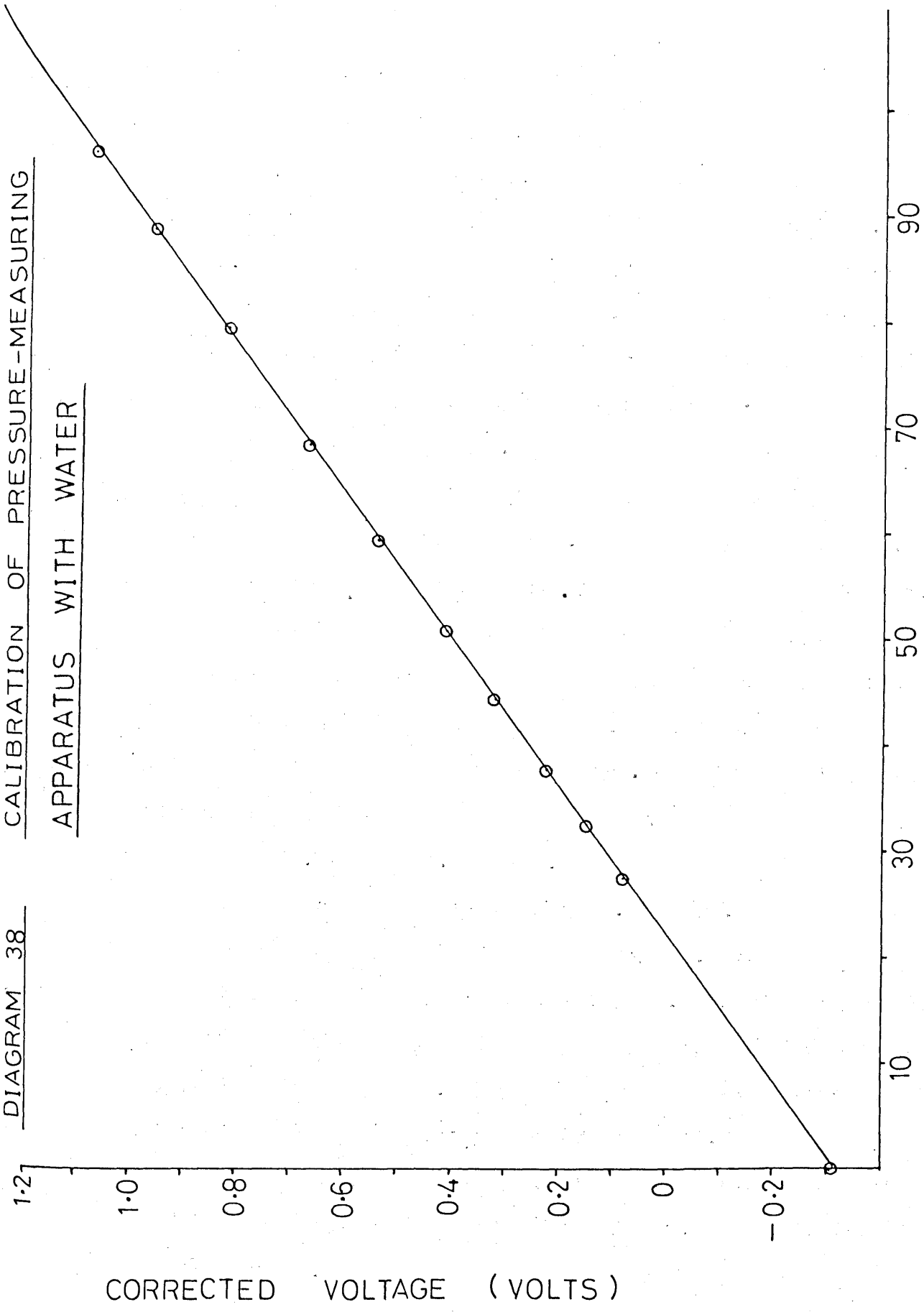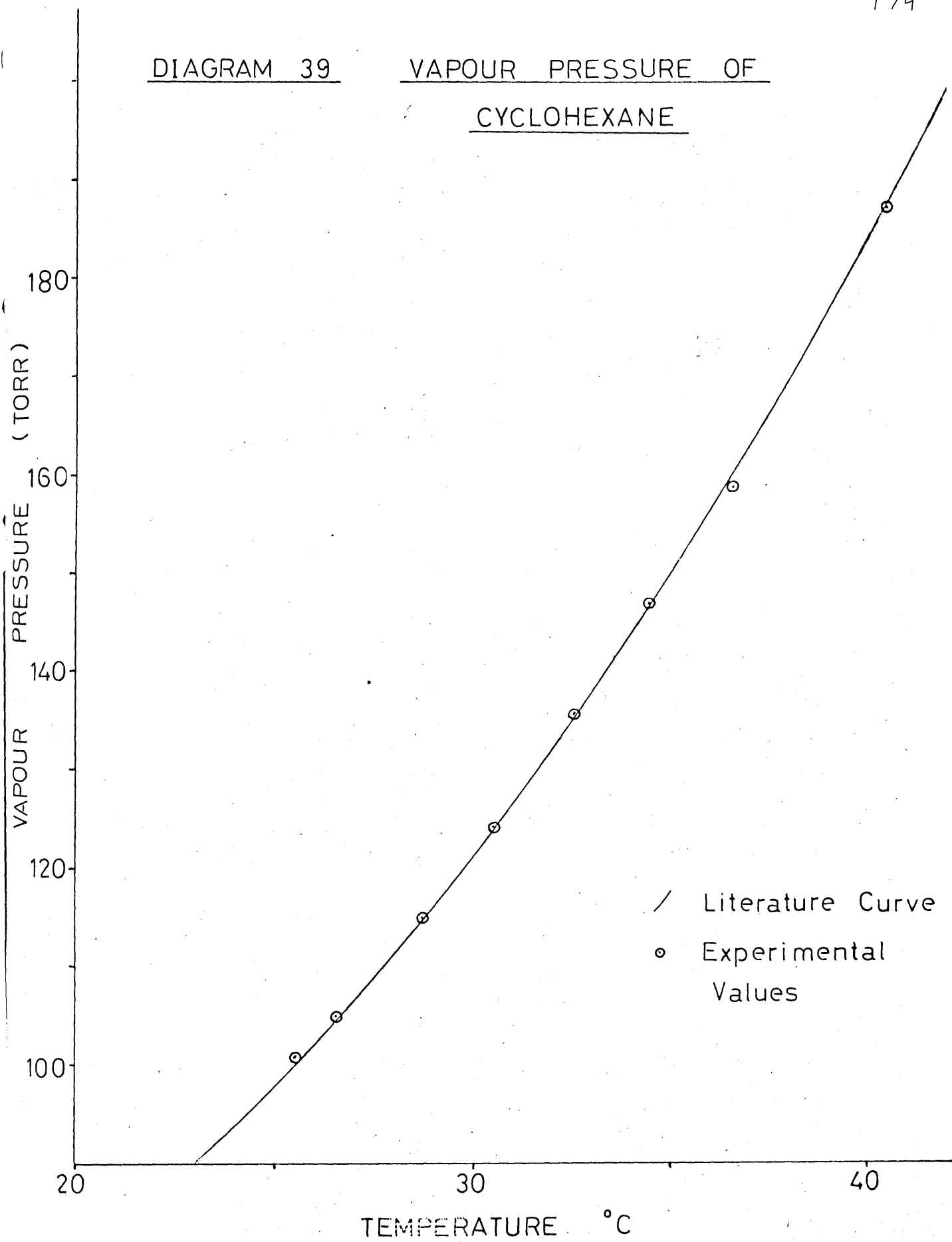
CORRECTED VOLTAGE (VOLTS)

PRESSURE (TORR)

178

DIAGRAM 39 VAPOUR PRESSURE OF CYCLOHEXANE

However, many of the $POCl_3/BCl_3$ pressures to be studied lay in a much lower range (0-20 torr) than the vapour pressures of cyclohexane. So, as a further check on the sensitivity of the apparatus at low pressures (1-6 torr), the vapour pressure-temperature curve was determined for a sample of pure propionic anhydride, already available in the laboratory. The results are plotted against the literature curve[133] in diagram 40. The literature values are from very old papers, so it is possible that their accuracy may be questioned to account for the discrepancy from the present values.

Two experiments were performed for phosphoryl chloride-boron trichloride gaseous mixtures, one in the range 25-55°C, the second from 10-40°C. Below 10°C, maximum permissible pressures (ca 3 torr) were so small that changes in pressure (ca 0.01 torr per degree or lower) could not be registered accurately. The vapour from the solid adduct was again used as the source of a 1:1 gaseous mixture of boron trichloride and phosphoryl chloride. The pressure-measuring apparatus was attached to the grease-free vacuum line (p. 53 diagram 10). The mixing vessel was filled with $POCl_3 \cdot BCl_3$, evacuated, weighed, and re-attached to the vacuum line. With the line evacuated and isolated from the pump, the adduct was opened to the pressure apparatus while being thermostatted slightly below the lowest temperature at which readings were to be taken (i.e. ca 20°C for the first experiment, ca 8°C for the

VAPOUR PRESSURE OF
PROPIONIC ANHYDRIDE

DIAGRAM 40
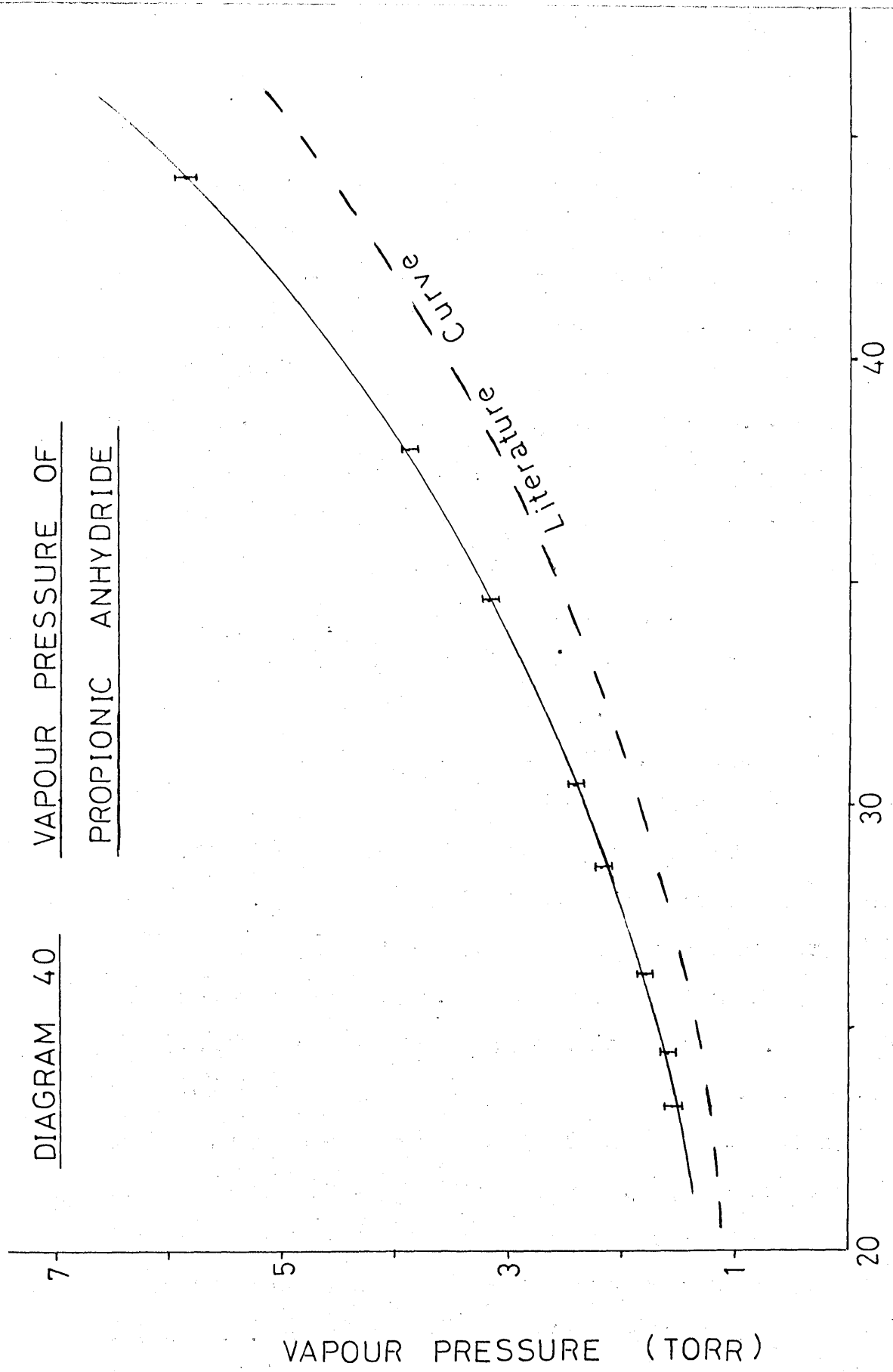
second). This was necessary to achieve as high a gas pressure as possible while avoiding the problem of possible condensation during the experiment. After allowing a few minutes for equilibration, the tap on the pressure apparatus was shut, and the remaining vapour condensed back into the mixing vessel, which could then be removed from the vacuum line and reweighed to determine the weight of vapour in the pressure vessel.

As the result of an accidental pressure shock between experiments one and two, the characteristics of the transducer were altered, necessitating recalibration. The sensitivity remained almost unchanged, but all voltage readings were decreased by a near-constant amount. Hence the calibration graphs in diagrams 37 and 38 apply only to the first experiment. The calibrations for the second experiment gave lines nearly parallel to the originals, but displaced by ca -0.149V.

RESULTS AND DISCUSSION

The results of the two experiments are given in table 29.

TABLE 29

PRESSURE V TEMPERATURE FOR GASEOUS $POCl_3$-BCl_3

MIXTURES

EXPERIMENT ONE : 0.0890 g $POCl_3 \cdot BCl_3$ used.

Voltage (V)	Compensated Voltage(V)	Pressure (torr)	Temperature (°C)
-0.006	-0.005	21.43	24.6
0.020	0.003	21.99	30.6
0.038	0.009	22.41	34.8
0.060	0.015	22.84	40.0
0.080	0.021	23.26	44.7
0.102	0.027	23.68	50.2
0.119	0.031	23.96	54.4
0.102	0.027	23.68	50.0
0.085	0.022	23.33	46.0
0.060	0.015	22.84	39.8
0.044	0.011	22.54	36.0
-0.003	-0.003	21.57	25.1

EXPERIMENT TWO : 0.0355g $POCl_3 \cdot BCl_3$ used.

Voltage (V)	Compensated Voltage(V)	Pressure (torr)	Temperature (°C)
-0.384	-0.342	8.13	10.1
-0.375	-0.343	8.06	13.3
-0.364	-0.341	8.20	16.7
-0.353	-0.339	8.34	20.2
-0.335	-0.337	8.48	25.6
-0.317	-0.334	8.65	30.7
-0.302	-0.333	8.76	35.4
-0.285	-0.331	8.90	40.4

Assuming an equilibrium

$$A(g) \rightleftharpoons B(g) + C(g)$$

then

$$p \text{ observed} = pA + pB + pC$$

and

$$\rho \text{ calculated} = \rho A + \tfrac{1}{2}(\rho B + \rho C)$$

where ρ observed = measured pressure

ρ calculated = pressure calculated from the simple
gas equation assuming total association

ρ A,B,C = partial pressure A,B,C.

This leads to

Degree of, $\alpha = \dfrac{\rho \text{ obs} - \rho \text{ calc}}{\rho \text{ calc}}$
Dissociation

Equilibrium, $K_\rho = \dfrac{(\rho \text{ obs} - \rho \text{ calc})^2}{2 \rho \text{ calc} - \rho \text{ obs}}$
Constant

The values for the degree of dissociation, α, thus calculated
are given in table 30.

These values for the degree of dissociation neglect any
deviations from Raoult's law due to Van der Waals' repulsive
forces. However, Brown[143,144] has shown that such interactions
can be neglected at pressures less than _ca_ 20 torr.

Calculated values for the equilibrium constant, K_ρ, are
not given because, as $(2\rho \text{ calc} - \rho \text{ obs})$ is so small in every
case (often less than the limits of error attached to ρ obs),
the wide limits of error which must be assigned to K_ρ render
it almost meaningless. These limits range from $\pm 40\%$ upwards,
corresponding to limits of -25% or more on $\ln K_\rho$; Hence
a graph of $\ln K_\rho$ against the reciprocal of the temperature to
determine ΔH is not sensible.

TABLE 30

DEGREE OF DISSOCIATION FOR $POCl_3 \cdot BCl_3(g)$

ρ obs(torr) ± 0.07	p calc (torr)	α ± 0.007	Temperature K
EXPERIMENT ONE			
21.43	10.89	0.968	297.8
21.57	10.91	0.977	298.3
21.99	11.11	0.979	303.8
22.41	11.26	0.990	308.0
22.54	11.31	0.993	309.2
22.84	11.45	0.995	313.0
22.84	11.48	0.990	313.2
23.26	11.63	1.000	317.9
23.33	11.67	0.999	319.2
23.63	11.82	1.003	323.2
23.68	11.83	1.001	323.4
23.96	11.98	1.000	327.6

ρ obs(torr) ± 0.07	p calc (torr)	α ± 0.02	Temperature K
EXPERIMENT TWO			
8.13	4.07	0.99	283.3
8.06	4.11	0.96	286.5
8.20	4.16	0.97	289.9
8.34	4.21	0.98	293.4
8.48	4.29	0.98	298.8
8.65	4.36	0.98	303.9
8.76	4.43	0.98	308.6
8.90	4.50	0.98	313.6

The results show that there is no association between
phosphoryl chloride and boron trichloride in the gas phase
above ca 45°C. Below this temperature, association is
possible, but sufficiently slight to have only a marginal
effect on the value of ΔH diss derived by Burg and Ross.
Further, in view of the relative agreement between the values
obtained by tensimetry and solution calorimetry in phosphoryl
chloride (Gutmann), it would seem that the solution hydrolysis
method (Finch, Gardner and Sen Gupta) ought to be reinvesti-
gated.

APPENDIX ONE

JUSTIFICATION OF THE PROPORTIONALITY OF THE DISPLACEMENT FROM ZERO ON CHART RECORDER AGAINST CHANGE IN RESISTANCE OF THERMISTOR

V volts

0 volts
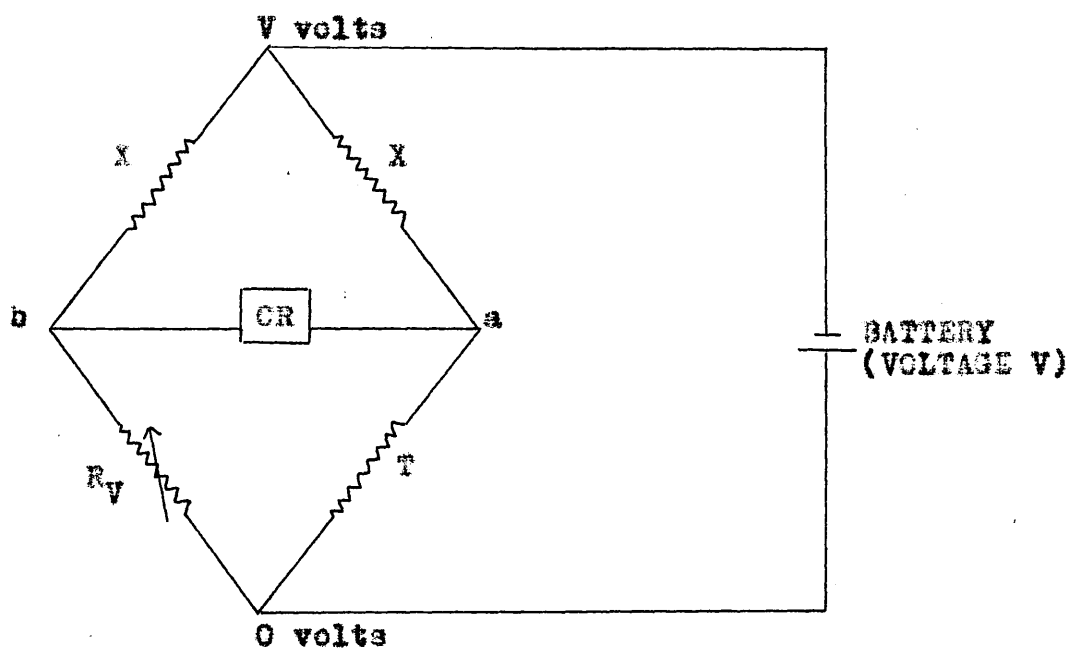
CR = Chart recorder

X = Matched pair of resistances ($\pm$ 1%) 4.3 kΩ

R_V = Variable resistance $(\equiv R_o)$

T = Thermistor resistance

Displacement from zero α Applied voltage (Maker's specifications)

Applied voltage = $V_a - V_b$

$$= \left(\frac{T}{T + X}\right)V - \left(\frac{R}{R + X}\right)V$$

As T changes, let $T = R_0 + \Delta R$ ($R_0 = T$ at balance)

$\therefore$ Applied voltage $= \left[\dfrac{R_0 + \Delta R}{R_0 + \Delta R + X}\right] V - \left[\dfrac{R_0}{R_0 + X}\right] V$

$$\dfrac{d \text{ (Applied voltage)}}{d \Delta R} = V\left[\dfrac{-R_0}{(R_0 + \Delta R + X)^2} + \dfrac{1}{(R_0 + \Delta R + X)} - \dfrac{\Delta R}{(R_0 + \Delta R + X)^2}\right]$$

$$= V\left[\dfrac{-R_0 + R_0 + \Delta R + X - \Delta R}{(R_0 + \Delta R + X)^2}\right]$$

$$= \dfrac{VX}{(R_0 + \Delta R + X)^2}$$

$$= \dfrac{VX}{(R_0 + X)^2 + 2\Delta R(R_0 + X) + (\Delta R)^2}$$

Since $\Delta R = \underline{ca}\ 5\ \Omega$

$R_0 = \underline{ca}\ 4900\ \Omega$

$X = 4.3\ k\Omega$

$\dfrac{d \text{ (Applied voltage)}}{d \Delta R} = \text{constant}$ to a very good approximation.

$(< 0.1\%)$

APPENDIX TWO

JUSTIFICATION OF LINEAR EXTRAPOLATION OF

RESISTANCE-TIME FORE- AND AFTER-PERIODS

$$\frac{dT}{dt} = K(T-T_j) + \omega \quad \text{Newton's law of cooling}$$

$$\text{where } T = \text{Temperature (K)}$$

$$t = \text{Time (minutes)}$$

$$T_j = \text{Jacket temperature (K)}$$

$$K, \omega = \text{constants.}$$

$$\therefore \frac{1}{K} \ln \left| [K(T-T_j) + \omega] \right| = t + c \quad \text{by integration}$$

$$\text{where } c = \text{integration constant.}$$

$$\therefore T = \frac{1}{K} e^{K(t+c)} - \frac{\omega}{K} + T_j$$

$$\text{But } T = \frac{B}{\ln \frac{R}{A}} \qquad \text{Thermistor relationship}$$

$$\text{where } A, B = \text{Thermistor constants}$$

$$R = \text{Thermistor resistance}$$

$$\therefore 1 = \ln \frac{R}{A} \left| \frac{e^{K(t+c)}}{BK} + \frac{T_j}{B} - \frac{\omega}{BK} \right|$$

Differentiating,

$$\frac{dR}{dt} = (\pm) \frac{R}{B} [\ln \frac{R}{A}]^2 e^{K(t+c)}$$

(Because of the modulus in $\ln | \ |$, the sign of $\frac{dR}{dt}$ must be determined separately).

Differentiating again,

$$\frac{d^2R}{dt^2} = \frac{R}{B^2} [(\ln {}^{R}/_{A})^4 + 2 (\ln {}^{R}/_{A})^3] e^{2K(t+c)}$$

$$- \frac{KR}{B} (\ln {}^{R}/_{A})^2 e^{K(t+c)}$$

For a straight fore- and after-period,

$$\frac{dR}{dt} = \text{constant}$$

and $$\frac{d^2R}{dt^2} = 0$$

Clearly, this is not rigorously true.   However, typical
values are [73], [113], [115]

$B = 3 \times 10^3 K$ $R_j = 5000 \,\Omega$

$A = 0.05 \,\Omega$ $\omega = 0.003 \ K \ min^{-1}$

$K = -0.01 \ min.^{-1}$ $R = 4950 \,\Omega$

Now, consider the after-period,

$$c = \frac{1}{K} \ln \left| \left[K \left(\frac{B}{\ln {}^{R_0}/_A} - \frac{B}{\ln {}^{R_j}/_A} \right) + \omega \right] \right|$$

where R_0 = Resistance at start of after-period

R_j = Thermistor resistance corresponding to
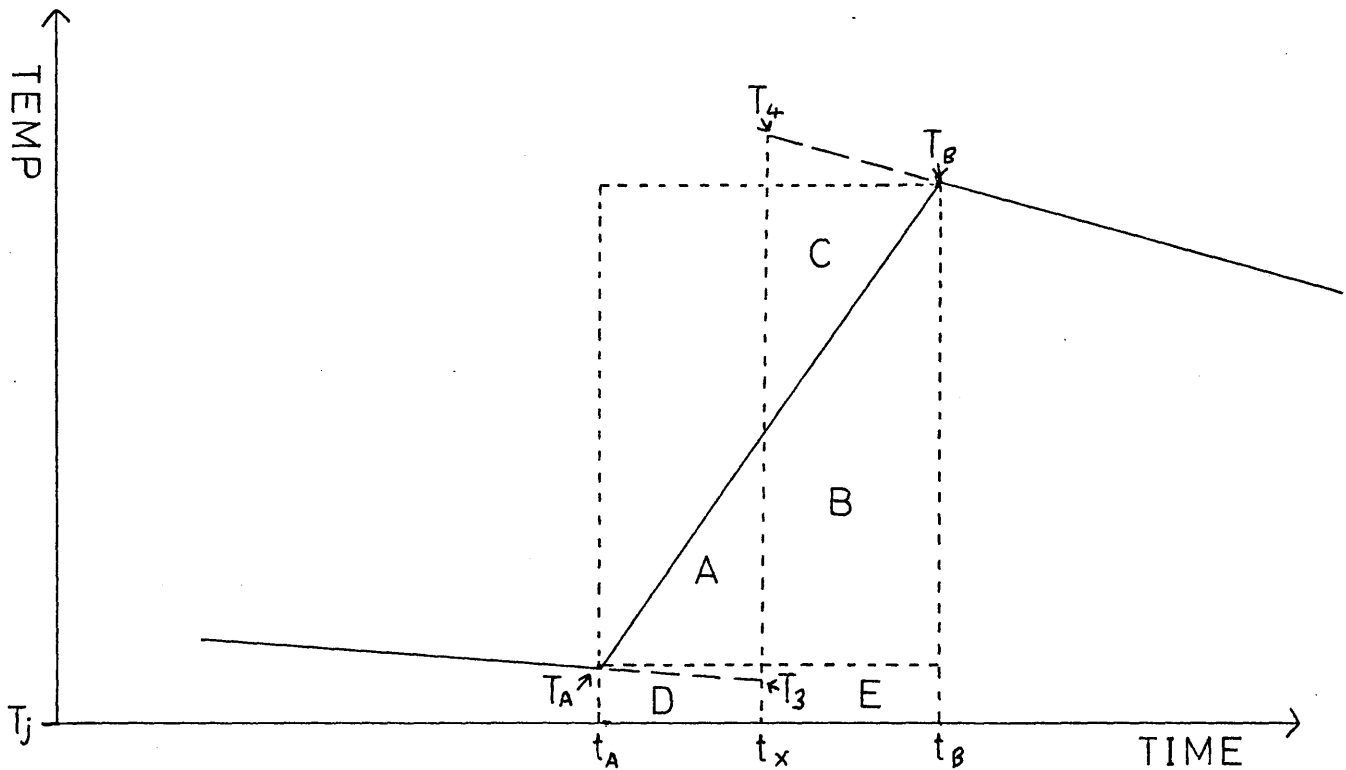   jacket temperature

$\therefore$ $c \simeq + 580$ min for after period

$$\therefore \quad \frac{dR}{dt} \text{ (at } t = 0) = \frac{-5 \times 10^3}{3 \times 10^3} (11.5)^2 (-0.003)$$

$$= \underline{\underline{0.7 \, \Omega \, \text{min}^{-1}}}$$

$$\frac{d^2R}{dt^2} \text{ (at } t = 0) = \frac{5 \times 10^3}{9 \times 10^6} [17500 + 3040] (5 \times 10^{-6})$$

$$- \frac{10^{-2} \times 5 \times 10^3}{3 \times 10^3} (11.5)^2 (3 \times 10^{-3})$$

$$= \underline{\underline{-0.006 \, \Omega \, \text{min}^{-2}}}$$

Normally, extrapolation is from $t = 0$ min to $t \simeq -2$ min for the after-period, during which time the slope of the resistance-time plot would change from, say, $0.700 \, \Omega \, \text{min}^{-1}$ to $0.712 \, \Omega \, \text{min}^{-1}$ giving a maximum error in the extrapolated resistance of $\pm 0.024 \, \Omega$. Since resistances can only be read accurately to $\pm 0.1 \, \Omega$, the possible error will be insignificant. Although the after-period only has been considered, similar results (with a smaller d^2R/dt^2 in fact) can be obtained for the fore-period.

In conclusion, it can be stated that the extrapolation of fore- and after-periods as straight lines is justified provided

(i) The lines are drawn using as short a section of the fore- and after-periods as practicable (ignoring the "overshoot" which occurs at the start of the after-period)

(ii) The extrapolation periods are less than five minutes

(iii) The apparatus design should be such as to minimise the values for dR/dt (i.e. K and ω both very small).

For the heating period $(t_A \longrightarrow t_B)$

$$\frac{dT}{dt} = K(T-T_j) + \omega \qquad \text{Newton's law}$$

$$= \frac{K \int_{t_A}^{t_B} (T-T_j)\, dt}{t_B - t_A} + \omega$$

(where $\frac{dT}{dt}$ is rate of change of temperature due only to heat loss to jacket, radiation, and heat of stirring.)

where $\displaystyle \frac{\int_{t_A}^{t_B} (T - T_J)\, dt}{t_B - t_A}$ $\equiv$ Mean temperature difference, $(T - T_J)$ over the heating period.

Now, total "corrected" temperature change on heating, ΔT is given by

$$\Delta T = T_B - T_A + \left(\frac{dT}{dt}\right)' (t_B - t_A)$$

where $\left(\dfrac{dT}{dt}\right)' \equiv$ Mean rate of temperature change during this period.

$$= T_B - T_A + K \int_{t_A}^{t_B} (T - T_J)\, dt + \omega (t_B - t_A)$$

$$= T_B - T_A + K(A + B + D + E) + \omega (t_B - t_A)$$

If t_x is a time such that $A = C$, then

$$\Delta T = T_B - T_A + K(B + C + E) + KD + \omega (t_B - t_A)$$

$$= T_B - T_A + K (T_B - T_J)(t_B - t_X)$$

$$+ K(T_A - T_J)(t_X - t_A) + \omega (t_B - t_A)$$

$$= T_B - T_A + [K(T_B - T_J)(t_B - t_X) + \omega (t_B - t_X)]$$

$$+ [K(T_A - T_J)(t_X - t_A) + \omega (t_X - t_A)]$$

$$\underline{\underline{\Delta T = T_B - T_A + (T_4 - T_3) + (T_A - T_3)}}$$

assuming the slope of the after-period is constant and equal to $K(T_3 - T_J) + \omega$, and similarly for the fore-period

$$\frac{dT}{dt} = K(T_A - T_J) + \omega$$

$$\therefore \quad \Delta T = T_4 - T_3$$

The resistances R_4 and R_3 corresponding to T_4 and T_3 are obtained by extrapolating the fore- and after-periods of the resistance-time graph to the time t_x i.e. To the mid-point of the heating period.

A recent paper by Gunn[145] draws similar conclusions to Appendices Two and Three on the use of thermistors, but from a different approach. The present techniques correspond to Gunn's "hybrid extrapolation method" (reference 145, p. 32, line 10). A typical reaction and calibration, where nearly equal temperature rises occur in each, would correspond to Gunn's set 5 and set 7 respectively (reference 145, p. 26, table 1).

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The enthalpy of hydrolysis and thermodynamic properties of carbonyl bromide

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By use of an adiabatic solution–reaction calorimeter, the standard enthalpy of formation of carbonyl bromide, $\Delta H_f^{\circ}(\text{COBr}_2, \text{l}, 298\ \text{K})$, was determined as $-(34.7 \pm 0.2)\ \text{kcal mol}^{-1}$.

1. Introduction

Evidence for the existence and nature of weak interactions between carbonyl halides and Lewis acids, e.g. aluminium halides, is difficult to interpret. Thus COCl_2 and Al_2Cl_6 are known[1] to form a solid complex, with no halogen exchange, as shown by radio-chlorine measurements.[2] Vibrational spectroscopic work in this laboratory,[3] however, indicates that halogen exchange between COCl_2 and Al_2Br_6 occurs, and further that there is (apparently catalytic) decomposition of COBr_2 by aluminium tribromide, following very weak complex formation. Clearly there are considerable differences between COBr_2 and COCl_2, and this has prompted the present determination of the standard enthalpy of formation of carbonyl bromide. Despite its easy synthesis and thorough spectroscopic characterization[4] thermodynamic data are limited to the results of an early[5] investigation of the equilibrium constant of the reaction:

$$\text{COBr}_2(\text{g}) = \text{CO}(\text{g}) + \text{Br}_2(\text{g}),$$

at 346.4 and 454.8 K, whence $\Delta H_f^{\circ}(\text{COBr}_2, \text{g}) = -23\ \text{kcal mol}^{-1}$.† Vapour pressure studies[6] corrected to 298 K, give $\Delta H_v = 7.4\ \text{kcal mol}^{-1}$, and hence[7] $\Delta H_f^{\circ}(\text{COBr}_2, \text{l}) = -30.4\ \text{kcal mol}^{-1}$. Limits of error are impossible to assign from the literature data. In the present work, a solution calorimetric method at 25 °C was employed for the measurement of the standard enthalpy of hydrolysis.

2. Experimental

MATERIALS

COBr_2 was prepared from carbon tetrabromide and concentrated sulphuric acid according to established procedures,[6] distilled, allowed to stand over mercury, re-distilled (normal boiling temperature 64.5 °C; literature[6] 64 to 65 °C), and

† Throughout this paper cal = 4.184 J, M = mol dm⁻³, and Torr = (101,325/760) kN m⁻².

stored in a grease-free vacuum line at liquid nitrogen temperature. For sampling, fractionation through -30 to $-96\,^\circ\text{C}$ was employed, the product being slightly discoloured. Samples were periodically checked by use of standard silver nitrate titrimetry on aqueous hydrolysates. It was found necessary to shake the liquid vigorously in stoppered flasks for not less than 40 min to ensure complete reaction. A typical result, using a 0.3339 g sample, was: Br(found), 84.6 per cent by mass; Br(calc.), 85.1 per cent by mass. Starch–iodide tests on the aqueous hydrolysate showed the free bromine content of $COBr_2$ to be less than 0.5 per cent by mass.

CALORIMETER AND PROCEDURE

The calorimeter was an all-glass Dewar type, containing 200 cm^3 of liquid, and similar to that previously reported,[8] but modified to operate adiabatically. The design of the automatic adiabatic control is the same (with minor modifications) as that employed in the Gallenkamp Adiabatic Bomb Calorimeter; full details are available elsewhere,[9] and will be forwarded on application. Before (i) and after (ii) runs using carbonyl bromide, the system was checked using the enthalpy of neutralization of tris(hydroxy-methyl)aminomethane (THAM) in excess aqueous 0.1 M hydrochloric acid. Results were: (i), -7.11 and (ii), -7.11 kcal mol^{-1}; literature:[10] $-(7.109 \pm 0.001)$ kcal mol^{-1}. For this calorimetric system the standard deviation of the mean for this reaction has been shown[9] to be ± 0.02 kcal mol^{-1}.

The reaction studied was:

$$COBr_2(l) + nH_2O(l) = CO_2(g) + \{2HBr + (n-1)H_2O\}(l)$$
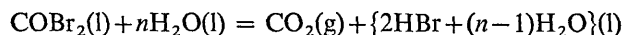
for which we denote the enthalpy change by ΔH_{hyd}. Thus

$$\Delta H_f^\circ(COBr_2, l) = \Delta H_f^\circ(CO_2, g) + 2\Delta H_f^\circ\{HBr \text{ in } \tfrac{1}{2}(n-1)H_2O\} - \Delta H_f^\circ(H_2O, l) - \Delta H_{hyd}.$$

The water in the calorimeter was pre-saturated with carbon dioxide to ensure that the evolved gas would be in its standard state. Thermal effects arising from the decreased solubility of carbon dioxide with the small temperature increase during reaction and also from the mixing of CO_2(aq) and HBr(aq) were ignored. The rate of hydrolysis of samples of about 0.3 g in 200 cm^3 of water was relatively slow ($t_{\frac{1}{2}} \approx 10$ min) and initial results, using a constant-temperature-environment calorimeter, were abandoned in favour of adiabatic measurements. Reproducible calorimetric results were obtained only after all contact between carbonyl bromide and grease was eliminated. Hence all-glass ampoules, sealed directly from a grease-free high-vacuum line (about 10^{-6} Torr) were employed to contain the carbonyl bromide, and no grease was used in the calorimetric head. Blank runs showed that the effect of heating the ampoule during sealing, and the enthalpy of ampoule breaking, were negligible. The amount of carbonyl bromide used in each run was measured by post-hydrolysis analysis. Corrections ΔH_{corr} for the carbonyl bromide present in the gas phase in the ampoule were applied.

3. Results

The results are given in table 1 from which we obtain $\Delta H_{hyd} = -(49.06 \pm 0.16)$ kcal mol^{-1}, the uncertainty interval being calculated as $\pm \{\sum \delta_i^2/n(n-1)\}^{1/2}$. Using

TABLE 1. Enthalpies of reaction, ΔH_{obs}, and enthalpies of hydrolysis, ΔH_{hyd}, of $COBr_2$ at $(25.0 \pm 0.1)\,°C$

Run	$\dfrac{m(COBr_2)}{g}$	$\dfrac{-\Delta H_{obs}}{kcal\ mol^{-1}}$	$\dfrac{\Delta H_{corr}}{kcal\ mol^{-1}}$	n	$\dfrac{-\Delta H_{hyd}}{kcal\ mol^{-1}}$
1	0.3723	49.01	0.05	5587	48.96
2	0.1930	49.06	0.12	10777	48.94
3	0.2242	49.49	0.11	9277	49.38
4	0.2168	48.37	0.09	9594	48.28
5	0.2248	48.56	0.11	9253	48.45
6	0.2553	49.16	0.10	8141	49.06
7	0.3342	49.68	0.06	6224	49.62
8	0.3862	49.61	0.06	4386	49.56
9	0.0845	49.61	0.30	24615	49.31

accepted values,[7] $\Delta H_f°(CO_2, g) = -(94.05 \pm 0.01)$ kcal mol^{-1}, $\Delta H_f°(H_2O, l) = -(68.315 \pm 0.001)$ kcal mol^{-1}, and $\Delta H_f°\{HBr$ in $\frac{1}{2}(n-1)H_2O\} = -(29.01 \pm 0.01)$ kcal mol^{-1} (mean value between $n = 5000$ and $n = 25000$), we obtain $\Delta H_f°(COBr_2, l) = -(34.70 \pm 0.21)$ kcal mol^{-1}.

4. Discussion

Statistical thermodynamic functions, based on the usual harmonic oscillator rigid rotor approximation, have been evaluated[4] for $COBr_2(g)$. Using these results in conjunction with the enthalpies presented above, the standard Gibbs energy and entropy of formation of $COBr_2$ (assumed ideal gas) have been calculated, and are compared with the corresponding functions for the analogous halides in table 2.

TABLE 2. Thermodynamic functions for $COX_2(g)$, $(X = F, Cl, Br)$, at 298.15 K

	COF_2	$COCl_2$	$COBr_2$
$-\Delta H_f°/kcal\ mol^{-1}$	151.7[a]	52.3[a]	27.3_0
$-\Delta G_f°/kcal\ mol^{-1}$	148.0[a]	48.9[a]	30.7_5
$-\Delta S_f°/cal\ K^{-1}\ mol^{-1}$	12.4	11.4	-11.5_6[b] $(10.7°)$

[a] From reference 7.
[b] Using data from references 4 and 7.
[c] Calculated taking the standard state of bromine as gas.

The apparently anomalous value of the standard entropy of formation of $COBr_2$ is due to the condensed standard state of bromine; as shown, this disappears if calculation using the appropriate value for bromine gas is adopted.

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